# SOME SUBSTITUTION REACTIONS OF METAL CARBONYLS

# THESIS

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WILLIAM HAMILTON STUBBS

Chemistry Department

The Royal College of Science and Technology

Glasgow

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## A C K N O W L E D G E M E N T S

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# SUMMARY

The first part of this study describes the substitution reactions of various metal carbonyl derivatives with phenylisocyanide. Qualitative studies of the substitution of halomanganese carbonyls have shown the ease of substitution to increase in the order iodide, bromide chloride. Complete stepwise replacement of the carbonyl groups in bromo-pentacarbonylmanganese has been achieved by variation of the reaction solvent and temperature.

Similar substitution reactions with the cyclopentadienyl metal carbonyl halides of iron and molybdenum have also shown the degree of substitution to vary with the electronegativity of the halogen used. Reduction of the mono substituted iron complex; iodo-carbonylphenylisocyanidecyclopentadienyliron has been found to give a dimeric complex containing a 'bridging' isocyanide group similar to the well established 'bridging' carbonyl groups of metal complexes.

Substitution reactions of methyl and phenylmanganesepentacarbonyl with phenylisocyanide have been found to give a mixture of mono and di-substituted derivatives of dimanganese decacarbonyl. This is in contrast to the reactions of the pentacarbonyls with carbon monoxide and amines, which are reported to give the acetyl and benzoyl derivatives.

The isocyanide analogues of tricarbonylcyclopentadienylmanganese and di(carbonylcyclopentadienylnickel) have been synthesised.

The second part of this study describes the various attempts which have been made to prepare heterocyclic derivatives of metal carbonyls, inwhich the heterocycle is bonded to the metal in an analogous manner to the bonding in metal-$\pi$-cyclopentadienyl compounds. Reaction of 2-methylpyrrole and manganese carbonyl has been found to give tricarbonyl-2-methylpyrrolylmanganese. Pyrrolyl potassium has been found to react with iodo-dicarbonylcyclopentadienyliron to give pyrrolylcyclopentadienyliron. Unsuccessful attempts were made to prepare the pyrrole analogues of ferrocene and nickelocene.

# C O N T E N T S

# INTRODUCTION

## PART I

Since the discovery of the first metal carbonyl, nickel tetracarbonyl, in 1888 by Mond and Langer,[1] the chemistry of metal carbonyls has expanded into a large field which has engaged the interest of experimental and theoretical chemists alike.[2,3,4,5] They occupy an unusual place in the metal complex field chiefly because of the ability of carbon monoxide to form stable complexes with transition metals in their lowest oxidation states. The resulting complexes, which are listed in Table 1 are electrically neutral, diamagnetic, except for vanadium hexacarbonyl, and quite volatile.

| Group V | Group VI | Group VII | Group VIII | | |
|---|---|---|---|---|---|
| $V(CO)_6$ | $Cr(CO)_6$ | | $Fe(CO)_5$ | | $Ni(CO)_4$ |
| | | $[Mn(CO)_5]_2$ | $Fe_2(CO)_9$ | $[Co(CO)_4]_2$ | |
| | | | $[Fe(CO)_4]_3$ | $[Co(CO)_3]_6$ | |
| | $Mo(CO)_6$ | $[Tc(CO)_5]_2$ | $Ru(CO)_5$ | | |
| | | | $Ru(CO)_9$ | $[Rh(CO)_4]_2$ | |
| | | | $[Ru(CO)_4]_3$ | $[Rh(CO)_3]_n$ | |
| | | | | $[Rh(CO)_{11}]_n$ | |
| | $W(CO)_6$ | | $Os(CO)_5$ | | |
| | | $[Re(CO)_5]_2$ | | $[Ir(CO)_4]_2$ | |
| | | | $Os_3(CO)_{12}$ | $[Ir(CO)_3]_n$ | |

TABLE I.

## Structure

In the metal carbonyls the metal atom normally attains the effective atomic number (E.A.N.) of the next inert gas.[6] This rule implies that all such compounds are inner orbital complexes, the inner d orbitals of the metal always being completely filled or used in $\sigma$-bonding. This tendency of the metal to attain an inert gas configuration is shown in table II for carbonyls of the first transition series which obtain the E.A.N. of krypton.

| Metal | Atomic Number | Carbonyl | Number of Electrons Donated by CO Groups. | E.A.N. |
|---|---|---|---|---|
| Cr | 24 | $Cr(CO)_6$ | 12 | 36 |
| Fe | 26 | $Fe(CO)_5$ | 10 | 36 |
| Co | 27 | $Co_2(CO)_8$ | 8 | 36 |
| Ni | 28 | $Ni(CO)_4$ | 8 | 36 |

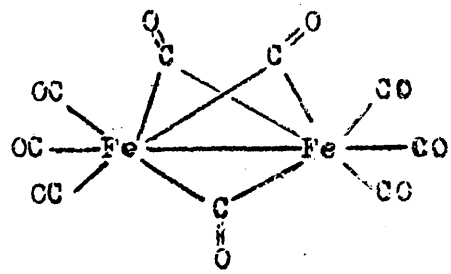
TABLE II

The stereochemistry of covalent complexes is a result of the formation of hybrid bond orbitals. This is most clearly seen in the case of nickel tetracarbonyl, which has been shown by electron diffraction studies to possess a tetrahedral structure.[7] The 4s and 4p-orbitals of the metal atom are hybridised resulting in four

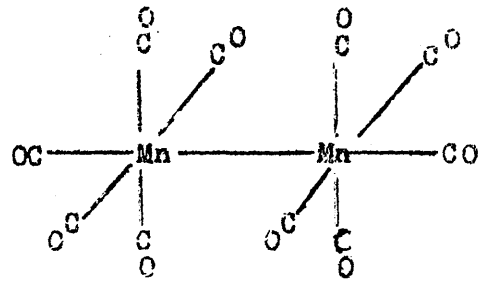
equivalent $sp^3$ hybrid orbitals directed towards the corner of a tetrahedron. Each carbonyl group forms a $\sigma$ bond with these orbitals whilst the overlap of the metal 3d orbitals and suitable orbitals of the carbonyl group enables $\pi$-bonding to occur. The octahedral structure[8] of the hexacarbonyls of chromium, molybdenum and tungsten are a result of $d^2sp^3$ hybridization. The structure and hybridization of iron pentacarbonyl is of particular interest because of the rare occurrence of penta-coordinated complexes and the existence of two equally probable structures, trigonal bipyramid and tetragonal pyramid, both of which can result from $dsp^3$ hybridization. The former structure is favoured by electron diffraction, Raman and infrared spectroscopic studies.[9-12]

A wide variety of polynuclear complexes occur in the metal carbonyls. Infrared spectroscopy has provided a powerful if not infallable method of structural investigation of such compounds. The elucidation of the structure of iron enneacarbonyl[13] (I) and the subsequent assignment of a band in the infrared at 1829 $cm.^{-1}$ to the 'bridging' or ketonic carbonyl[14] led to further investigation of similar compounds. Cobalt octacarbonyl has been shown to have two bridging carbonyls and six terminal carbonyls.[15] The other

dimeric carbonyls, dimanganese decacarbonyl (II) and dirhenium decacarbonyl, have however nearly regular octahedral coordination.[16]



I



II

Whereas the bridging carbonyls absorb in the range 1750 to 1850 $cm.^{-1}$ in the infrared, which is similar to normal organic ketone groups, terminal carbonyls generally absorb in the range 1900 to 2100 $cm.^{-1}$. Variations of the terminal carbonyl stretching frequencies are however observed when the carbonyls are substituted by ligands. The donation of electrons by the ligand to the metal atom causes a formal negative charge to reside on the metal atom which it tends to dissipate in accordance with Pauling's electroneutrality principle. This dissipation of charge may occur in two ways; either by back donation of the 3d electrons of the metal to the entering ligand or by increasing the bond order

in the metal carbonyl system. The latter effect results in a lowering of the carbonyl stretching frequency in the infrared and is at a maximum when the ligand has little or no ability to accept back donation from the metal. When the ligand has orbitals available for acceptance of d electrons, the trend is reversed and the carbonyl frequencies are shifted to a higher value. This is illustrated in table III.[109]

| Compound | cm.$^{-1}$ 2100 | 1900 | 1700 |
|---|---|---|---|
| $Py_3Mo(CO)_3$ | | | |
| $(PPh_3)_3Mo(CO)_3$ | | | |
| $(AsPh_3)_3Mo(CO)_3$ | | | |
| $(SbPh_3)_3Mo(CO)_3$ | | | |
| $(PCl_3)_3Mo(CO)_3$ | | | |
| $(PhPCl_2)_3Mo(CO)_3$ | | | |
| $(Ph_2PCl)_3Mo(CO)_3$ | | | |
| $(PPh_3)_3Mo(CO)_3$ | | | |

TABLE III

Substitution Reactions in Metal Carbonyls.

Reactions of metal carbonyls fall into two main categories; displacement of carbon monoxide without change in the oxidation state of the metal atom, and displacement with disproportionation. The former type is more common and has been effected by a variety of ligands, e.g. phosphines, amines, hydrocarbons etc. This work, and hence this review, is concerned principally with such reactions of metal carbonyls with isocyanides.

Isocyanide Derivatives of Metal Carbonyls.

Isocyanides together with carbon monoxide are among the very few substances with a lone pair of electrons on a carbon atom. Their structure can be considered to be a hybrid of the two resonance structures (III) and (IV). Structure (III) is in agreement with a bent molecule and

$$R - \overset{-}{N} = C \qquad R - \overset{(+)}{N} \equiv \overset{(-)}{C}$$

(III) (IV)

structure (IV) with a linear molecule. No evidence is available on the linearity of the aryl isocyanides. However measurements of the C-N-C angle in methylisocyanide show the molecule to be linear which suggests that structure (IV) is the more important.[132]

The lone electron pair on the carbon atom and the ability of the carbon atom to accept back donation of d-electrons enables isocyanides to act as ligands in a similar manner to carbon monoxide. An exact parallelism with carbon monoxide is however not observed. This may be attributed to the lesser electronegativity of the nitrogen atom in isocyanides in comparison to the oxygen atom in carbonyls. This results in the relative favouring of structure (VI) over structure (V) in the metal isocyanide complexes.

$$M = C = N - R \qquad M - C \equiv N - R$$
$$\text{(V)} \qquad \overset{(-)}{\text{(VI)}} \quad \overset{(+)}{}$$

In the metal carbonyl complexes, structure (VII) predominates over structure (VIII).

$$M = C = O \qquad M - C \equiv O$$
$$\text{(VII)} \qquad \overset{(-)}{\text{(VIII)}} \quad \overset{(+)}{}$$

Thus isocyanides tend to stabilize low valency states, but to a smaller extent than carbon monoxide.

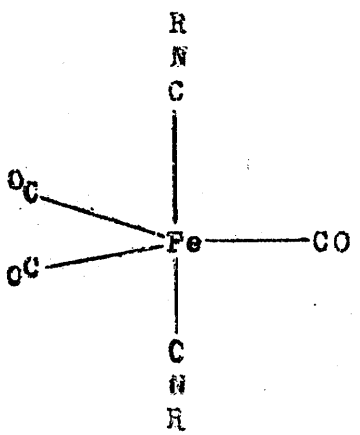
<u>Displacement by Isocyanide without Change in the Oxidation State of the Metal Atom.</u>

The preparation of isocyanide derivatives of nickel carbonyl by Hieber[18] was the first of many reactions to demonstrate the similarity between carbon monoxide and

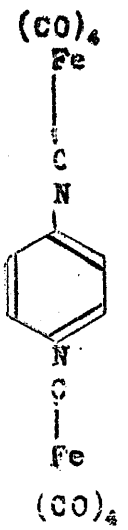
isocyanides in metal complexes.

Complete replacement of carbon monoxide from unsubstituted metal carbonyls occurs only with nickel tetracarbonyl, and even in this case aryl isocyanide must be used. With methylisocyanide the reaction stops to give tris(methylisocyanide)carbonyl nickel.

With iron pentacarbonyl substitution of up to two moles of carbon monoxide occurs to give bis(isocyanide) tricarbonyliron.[19] Replacement of the two carbonyls by one mole of ethylisocyanide and one mole of methylisocyanide yields the same complex irrespective of the order of use of the different isocyanides. This shows that the isocyanide ligands must be in equivalent positions. Recent evidence[110] further suggests that they are in trans positions to each other (IX)




IX




X

An interesting derivative (X) of iron pentacarbonyl has been prepared using para-di-isocyanobenzene.[19] Attempts to prepare the monomeric tricarbonyl derivative did not succeed due to the linearity of the di-isocyanide molecule.

Displacement of only one carbonyl group by isocyanides from the hexacarbonyls of chromium, molybdenum and tungsten has been achieved.[20] Higher substitution derivatives of chromium and molybdenum carbonyls have been isolated by replacement of other ligands from carbonyl complexes e.g. the replacement of the arene group from cycloheptatriene tricarbonylchromium by isocyanide gives tris(phenylisocyanide) tricarbonylchromium.[21]

No displacement reactions with dimeric carbonyl without change in the oxidation state are known. The special case of cobalt carbonyl is discussed later.

The incomplete substitution of the metal carbonyls is due to the increasing strength of the metal-carbonyl bond on introduction of a poorer electron accepting ligand. This is shown by the higher temperature required before replacement of a second carbonyl group with isocyanide from iron penta-carbonyl.

Displacement with Disproportionation

This occurs in the reaction between cobalt carbonyl and isocyanide. Originally the product of the reaction was reported[22] as being $[Co(CO)(CNAlkyl)_3]_2$ or $Co_2(CO)_3(CNAlkyl)_3$. This was subsequently disproved[23] and the complex identified as $[Co(CO)_4]^-[Co(CNR)_3]^+$ by the reaction of sodiocobalt tetracarbonyl with pentaisocyanide cobalt(I) iodide to give an identical product to that isolated from the substitution reaction.

Isocyanide Complexes of Transition Elements.

The transition elements of Groups VI, VII, and VIII generally form more than one type of isocyanide derivative corresponding to the various oxidation states. Lower valency state derivatives are usually prepared by treatment of the metal salts with isocyanide and a reducing agent. Table IV gives the lowest valency state derivatives

| Group VIA | Group VIIA | Group VIII | | |
|---|---|---|---|---|
| $Cr(CNR)_6$ | $Mn(CNR)_5I$ | $Fe(CNR)_4Cl_2$ | $Co(CNR)_5I$ | $Ni(CNR)_4$ |
| $Mo(CNR)_6$ | | $Ru(CNR)_4Cl_2$ | $Rh(CNR)_5I$ | $Pd(CNR)_4$ |
| $W(CNR)_6$ | $Re(CNR)_6I$ | | | $Pt(CNR)_4$ |

TABLE IV

The Group VIA derivatives[24,25,26] are stable crystalline complexes akin to their carbonyl analogues. The univalent manganese complex on oxidation yields the divalent $Mn(CNR)_6^{++}$ cation.[27] The compounds obtained by direct reaction of iron(II) salts and isocyanide contain at most four molecules of isocyanide, the hexaisocyanide derivatives are obtained by alkylation of hexacyanoferrates.

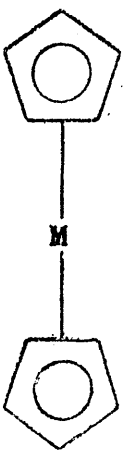
The higher valency state derivatives are generally formed by the alkylation of complex cyanides. An excellent review covers all these compounds comprehensively.[28]

# INTRODUCTION

## PART II

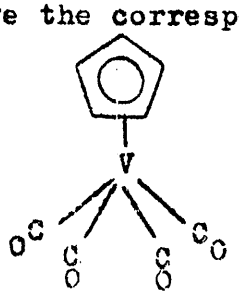
Cyclopentadienylmetalcarbonyls.

Intensive research in the decade following the discovery of ferrocene (XI, M = Fe) in 1951[29,30] resulted in the synthesis of numerous organometallic compounds incorporating the large majority of transition elements. Dicyclopentadienyl compounds of the type $(C_5H_5)_2M$ (XI) are now known for all the metals of the first transition series from titanium to nickel.[31]

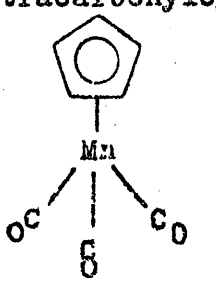



XI

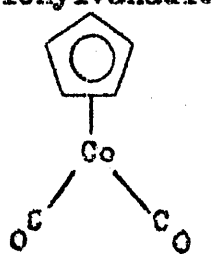
Carbon monoxide was found to displace one cyclopentadienyl group from dicyclopentadienyl vanadium[32] (XI, M = V) to give the corresponding tetracarbonylcyclopentadienylvanadium.




XII




XIII

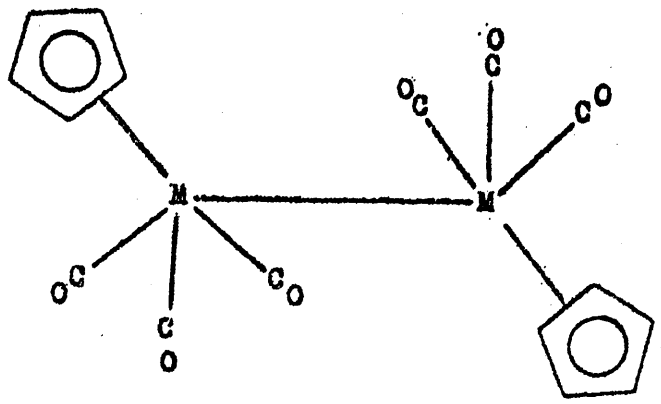



XIV

Shortly afterwards the corresponding cyclopentadienyl derivatives of cobalt carbonyl[33,34] (XIV) and manganese carbonyl[33,35] (XIII) were prepared in a similar fashion. Tricarbonylcyclopentadienylmanganese (XIII) is the most stable of these compounds, and whereas further treatment with carbon monoxide of dicarbonylcyclopentadienylcobalt (XIV) leads to cobalt carbonyl, the manganese complex (XIII) does not readily react further with carbon monoxide.

Tricarbonylcyclopentadienylmanganese (XIII) has been shown[36] to undergo electrophilic substitution reactions typical of an aromatic system. Competitive experiments[36] have shown that compound (XIII) and tricarbonylmethylcyclopentadienyl manganese (XV) possess a higher reactivity than benzene in electrophilic substitution reactions.

The search for alternative routes to dicyclopentadienyl complexes resulted in the discovery of other compounds containing only one cyclopentadienyl group bonded to a transition metal. Wilkinson[37] in an attempt to prepare the molybdenum and tungsten analogues of ferrocene by the reaction of the metal hexacarbonyls with cyclopentadiene isolated the dimeric species, bis(tricarbonylcyclopentadienyl metal) (XVI, M = Mo or W). The chromium analogue (XVI, M = Cr) was isolated later using milder conditions.[38]



(XVI)

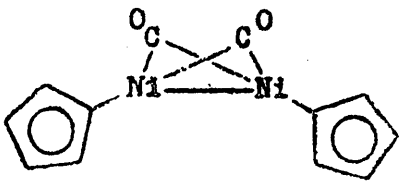
Di(carbonylcyclopentadienylnickel)[39] (XVII) is obtained from the reaction of dicyclopentadienylnickel and nickel carbonyl. Prolonged heating causes the reaction to proceed to the trimeric species.

$$Ni(CO)_4 + (C_5H_5)_2Ni \rightarrow 2CO + [C_5H_5Ni(CO)]_2 \rightarrow CO + (C_5H_5)_3Ni_3(CO)_2$$

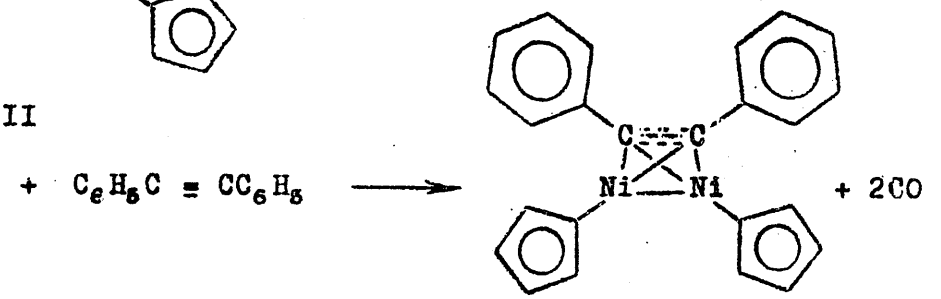
The dimer (XVII) has been reported[40] to react with diphenylacetylene, losing two molecules of carbon monoxide, to give diphenylacetylene di(cyclopentadienylnickel) (XVIII). This suggests that compound (XVII) possesses a 'folded structure', i.e. with two bridging carbonyl groups lying in intersecting planes.

The only other symmetrical dimeric cyclopentadienyl carbonyl complexes known are those of the iron triad, $[C_5H_5M(CO)_2]_2$. Iron carbonyl and cyclopentadiene[36,41] react at

135° to give di(carbonyl-μ-carbonylcyclopentadienyliron) (XIX) which has a structure[42] in which the two bridging

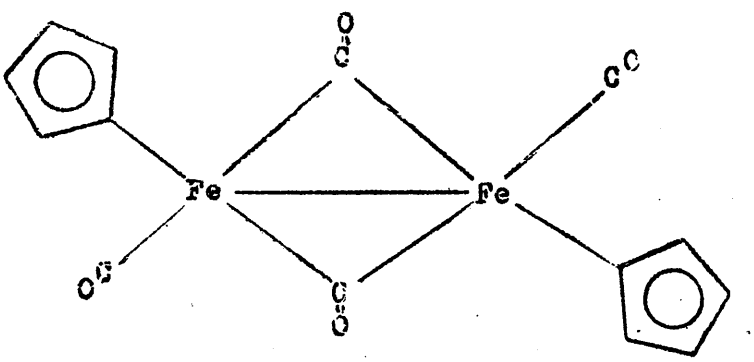


XVII



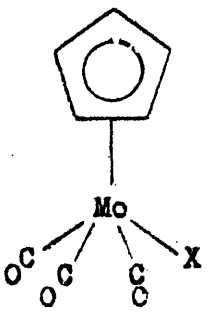
XVIII

carbonyl groups are coplanar. The ruthenium derivative[80] has a similar structure unlike the osmium analogue[81] in which there are no bridging carbonyls.

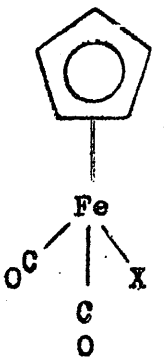


XIX

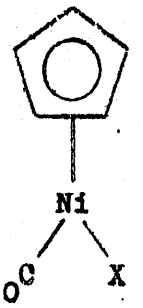
The halides derived by oxidation of the dimeric cyclopentadienylmetal carbonyls attain their E.A.N by behaving as covalent complexes (XX, XXI, XXII).




XX



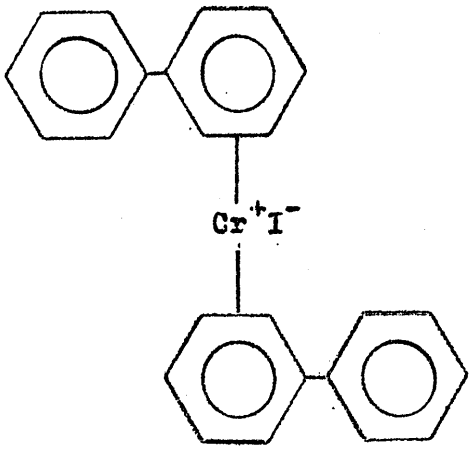

XXI



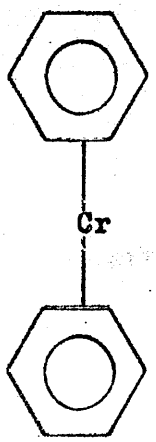

XXII

Arene Metal Carbonyls.

The discovery of $\pi$-cyclopentadienyl derivatives of transition metals led to the re-examination of Hein's polyphenylchromium complexes by Zeiss and Tsutsui.[43] They proposed structure (XXIII) for Hein's so-called 'tetraphenylchromium iodide'. The dibenzenechromium cation was also identified, by Zeiss and Herwig,[66] as being one of the reaction products and this was reduced to dibenzenechromium (XXIV). Evidence for the six-fold symmetry of this compound has been reported.[67]



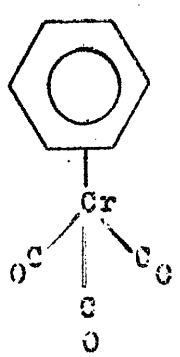

XXIII




XXIV

The direct preparative route to the arene chromium compounds is due to Fischer and Hafner[44,45] and involves the reaction of the aromatic hydrocarbon with chromic chloride in the presence of anhydrous aluminium chloride and aluminium powder at high temperature. Fischer has extended this work to the preparation of the bis-arene compounds of other transition metals.[46,47,48,49,50]

Reaction of dibenzene chromium (XXIV) with chromium hexacarbonyl led to the synthesis of tricarbonylbenzenechromium (XXV)[51,52]




XXV

A more general method of preparation, devised independently by Fischer,[68,69] Natta[53] and Whiting[54] is to heat the aromatic compound with chromium hexacarbonyl under reflux or in an autoclave under pressure in a solvent such as diglyme:-

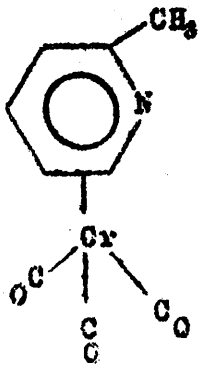
$$Ar + Cr(CO)_6 \xrightarrow{\text{diglyme}} ArCr(CO)_3 + 3CO$$

It has been shown[54] that the metal carbonyl residue results in electron withdrawal from the arene system. This causes decreased reactivity of the arene group towards electrophylic reagents and conversely an increase in reactivity towards nucleophilic reagents.

Heterocyclic Metal Carbonyls.

The main hindrance to the preparation of many heterocyclic transition metal compounds in which the heterocyclic ring is bound to the metal atoms in a similar fashion to the bonding in $\pi$-cyclopentadienyl and arene metal complexes, is the donor function associated with the presence of lone pairs of electrons on the hetero atoms. This is illustrated by the reactions of pyridine with metal carbonyls. Pyridine whilst possessing a sextet of $\pi$-electrons also contains a lone pair of electrons on the nitrogen atom. Reactions with the hexacarbonyls of chromium, molybdenum, and tungsten result in the displacement of up to three molecules of carbon monoxide by a similar number of molecules of pyridine to form mixed carbonyl pyridine metal complexes in which the pyridine molecule is bonded to the metal atom by a dative $\sigma$ bond.

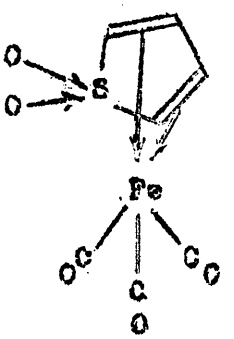
The blocking of the donor function of the nitrogen atom in pyridine by forming the corresponding N-methyl-pyridinium iodide, has given rise to salts, such as $[C_5H_5N^+Me][ICr(CO)_5^-]$ on reaction with chromium carbonyl.[55,56] Pyrolysis of this salt has yielded tricarbonyl-C-methyl-pyridinechromium (XXVI).



XXVI

Blocking of the donor function of the nitrogen atom in pyridine has also been achieved by steric hindrance caused by substitution on the ring system. Whiting[70] has shown that 2,4,6-trimethylpyridine reacts with chromium carbonyl to give tricarbonyl-2,4,6-trimethylpyridinechromium (XXVII).

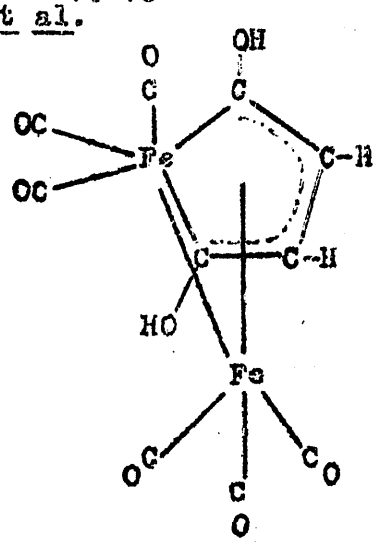
Several other systems containing a heterocycle bonded to a transition metal have been prepared. Iron pentacarbonyl undergoes displacement of two molecules of carbon monoxide by thiophenedioxides to give compounds of the type tricarbonylthiophenedioxideiron[58] (XXVIII).



XXVIII

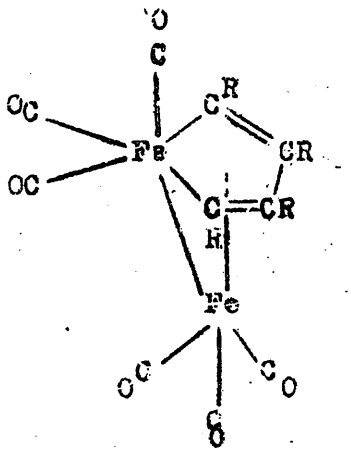
Novel heterocyclic derivatives, in which the metal atom is incorporated in the heterocycle, have been isolated from the reactions of iron carbonyls and acetylenes.

The reaction of iron carbonyl with acetylene in aqueous alcohol under pressure has been reported by Reppe[72] as giving a product, $C_{11}H_7O_3Fe$. This compound was later reformulated[73] as $C_{11}H_6O_3Fe$, but its structure is not yet definitely known. The reaction of alkaline solutions of iron carbonyl and acetylene were also described by Reppe who formulated the reaction product as $C_{10}H_4O_8Fe_2$. The structure (XXIX) of this compound has been elucidated by X-ray measurements[61] of its dimethyl derivative, obtained from but-2-yne and iron carbonyl, the presence of the fragment $-\overset{OH}{C} - CR - CR - \overset{OH}{C} -$ in the complex having been shown previously by Jones et al.[74,75]

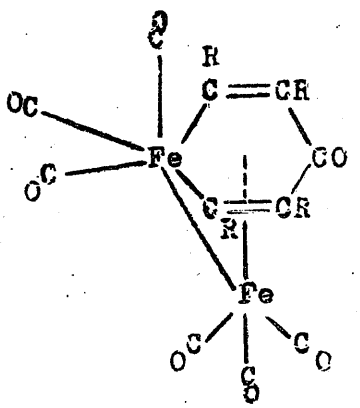



XXIX

Hubel and his co-workers[58,59,71,76-78] have extensively investigated the reactions of the three iron carbonyls with a variety of acetylenes, but principally with phenylacetylene and tolane. These have been found to give two main products with the general formula $(C_2R_2)_2Fe_2(CO)_6$[59,79] and $(C_2R_2)_2Fe_2(CO)_7$,[77,79] the former having a structure (XXIXa) related to the butyne-2-complex and the latter a structure as shown in (XXIXb). Also identified from these reactions were tropone and cyclopentadienone iron carbonyls together with many other compounds depending on the acetylene and the conditions used.



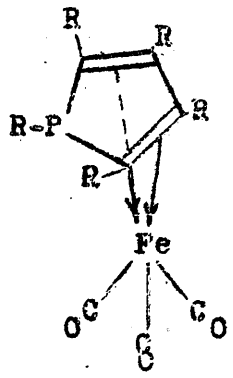
XXIXa



XXIXb

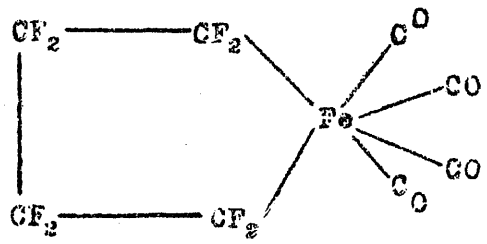
Compound (XXIXa; R = H) has also been isolated from the reaction of iron pentacarbonyl and thiophene.[62] Reactions of compound (XXIXa; R = Ph) with dichlorophenylphosphine gives

tricarbonylpentaphenylphospholeiron[71] (XXX; R = Ph)



XXX

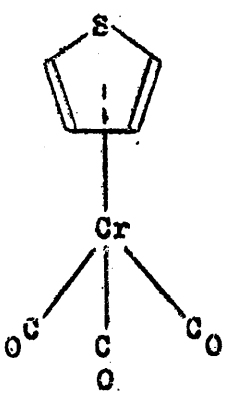
Tetrafluoroethylene and iron pentacarbonyl have been shown[63] to react to give compound (XXXI) in which the iron atom is bonded to the organo group by two $\sigma$-bonds



XXXI

Prior to commencing this work no compounds had been reported in which the heterocyclic ring system is bonded to a transition metal in an analogous manner to the bonding in $\pi$-cyclopentadienyl metal compounds. The only reported attempt to prepare such a compound was by Fischer,[64]

when he found that $[Ni(NH_3)_4](C_4H_4N)_2$ did not undergo reaction to give dipyrrolylnickel, $(C_4H_4N)_2Ni$, unlike the cyclopentadiene derivative, $[Ni(NH_3)_6](C_5H_5)_2$ which on heating is converted to -bis(cyclopentadienylnickel).[65] Fischer and Öfele[64] found however that thiophene and chromium carbonyl react together to give tricarbonylthiophenechromium (XXXII) in which the heterocyclic residue behaves as a six $\pi$-electron arene system.




XXXII

# THEORETICAL

## PART I

## ISOCYANIDE DERIVATIVES OF METAL CARBONYLS

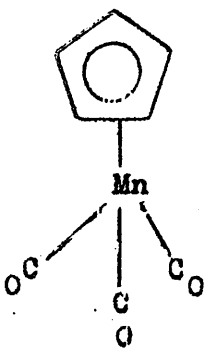
Examination of the structure of isocyanides shows that they possess several properties which render them useful as ligands in substitution reactions of metal carbonyls. The ability of isocyanides to donate a lone pair of electrons from an atom of low electronegativity is coupled with the availability of orbitals on the donor atom. This enables the ligand to accept back-donation of d-electrons from the central metal atom resulting in the greater stability of the complexes. Unlike triaryl phosphines, arsines etc., isocyanides are not bulky groups. This diminishes possible stereochemical problems which would tend to inhibit substitution of metal carbonyls. Finally, the presence of isocyanide groups in a metal complex is easily discernible by their absorption in the infrared spectrum around 2100 $cm.^{-1}$ due to the stretching frequency of the C≡N entity. This enables further conclusions to be made concerning the structure and bonding in mixed complexes.

This work describes the results of experiments designed to investigate the extent of the similarity between isocyanides and carbonyls as ligands in transition metal complexes. Phenyl-isocyanide was used exclusively in these reactions for two main reasons. Aryl isocyanides are less toxic[82-85] than alkyl isocyanides and form metal complexes which are more stable than alkyl isocyanide metal complexes.

Isocyanide complexes of manganese

The only reported isocyanide complexes of manganese are the hexakisisocyanide derivatives of Mn(I)[92] and Mn(II)[93], and the bisisocyanide derivatives of halopentacarbonylmanganese, $XMn(CO)_5$, (XXXIII)[86-89, 94]

The isolation of tricarbonylcyclopentadienylmanganese (XIII) suggested the probability of an isocyanide analogue.



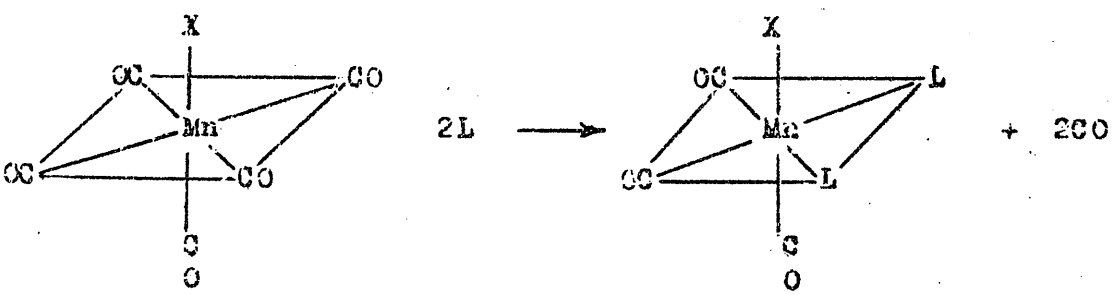

XIII

Substitution of compound (XIII) by isocyanide occurs only under vigorous conditions and gives only the mono substituted derivatives, dicarbonylisocyanidecyclopentadienyl manganese (XXXIV)[95].

Compound (XIII) has been prepared by the reaction of bromopentacarbonylmanganese (XXXIII, X = Br) with cyclopentadienylsodium[96] This reaction presumably proceeds via the σ-bonded intermediate, pentacarbonylcyclopentadienylmanganese, which loses two molecules of carbon monoxide to give the

π-bonded complex (XIII). It was found that hexakis(phenylisocyanide)manganese(I) iodide (XXXV) also underwent reaction with cyclopentadienylsodium to give tris(phenylisocyanide)cyclopentadienyl manganese (XXXVI), a yellow crystalline substance which unlike the carbonyl analogue does not readily volatilise.

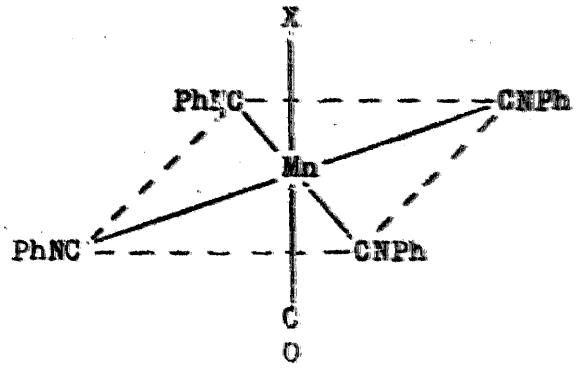
In order to investigate alternative routes to complexes of this type, the substitution of halomanganese carbonyls (XXXIII, X = Cl, Br, I) with isocyanide was investigated. Hieber *et al.* have reported[8] that compounds (XXXIII) undergo substitution by a variety of ligands, including isocyanides, to give the corresponding disubstituted derivatives $Mn(CO)_3L_2X$ (XXXVII). *Cis* structures were assigned to these complexes by Wilkinson *et al.*[97] and the absence of any higher substitution products was explained on the basis of the increased back-bonding from the metal to the remaining carbonyl groups on introduction of ligands with poorer acceptor properties. More recently Basolo *et al.*[90] have synthesised both *cis* and *trans* isomers of several disubstituted derivatives.




XXXIII XXXVII

Phenylisocyanide was found to react with bromopentacarbonylmanganese (XXXIII, X = Br) to give bromotricarbonylbis(phenylisocyanide)manganese (XXXVII, L = $C_6H_5NC$, X = Br) using refluxing ethanol as solvent. This compound shows absorption in the metal carbonyl stretching frequency region of the infrared at 2053 $cm.^{-1}$, 2004 $cm.^{-1}$ and 1954 $cm^{-1}$ (all strong). This is very similar to the reported carbonyl absorption frequency of cis- bromotricarbonylbis(triphenylphosphite) manganese[90] (XXXVIII) [viz. 2053 $cm.^{-1}$, 2000 $cm.^{-1}$ and 1949 $cm.^{-1}$ (all strong)] and suggests that the bisisocyanide derivative has structure (XXXVII, L = $C_6H_5NC$).

The use of tetrahydrofuran as solvent was found to increase the ease of substitution of bromopentacarbonylmanganese by phenylisocyanide. The major product from the reaction was found to be bromocarbonyltetrakis(phenylisocyanide)manganese (XXXIX). A small quantity of bromopentakis(phenylisocyanide) manganese (XL) was also isolated. Excess of compound (XXXIX) over compound (XL) can be explained by the assignment of structure (XLI) to the tetrakisisocyanide derivative. The carbonyl in this structure is trans to the bromine atom and as a result is more strongly bonded to the manganese atom than the other original four carbonyl groups due to the greater $\pi$-bonding character of the carbonyl in contrast to the halogen.




XLI

Consequently the low yield of the penta-substituted derivative is not surprising. This result is in agreement with kinetic studies[89] on bromo-pentacarbonylmanganese which show that one carbonyl group is less labile than the remaining four groups.

In order to investigate the role of the solvent in this reaction, bromo-pentacarbonylmanganese alone was heated in refluxing tetrahydrofuran. It was found that a volume of gas was evolved which was equivalent to the displacement of four molecules of carbon monoxide. This suggests that the substitution reaction proceeds via an intermediate tetrahydrofuran complex which in the presence of a donor-acceptor ligand reacts further to give complexes of the type (XXXIX) and (XL).

Kinetic studies[89] on halo-pentacarbonylmanganese systems show that the rates of carbon monoxide exchange decrease in the order; $Cl \gg Br > I$. This is explained by the decreasing electronegativity of the halogen atoms. The flow of electron density away from the manganese atom towards the carbonyl

groups is enhanced by a smaller effective positive charge on the manganese. Since iodine has the least electronegativity it renders the manganese the least positive and promotes a manganese-carbon double bond and consequently more carbon-oxygen double bond character. This is illustrated by the absorption in the carbonyl region of the infrared (Table V)[97]

| Carbonyl Halide | CO Stretching Mode ($cm^{-1}$) |
|---|---|
| $IMn(CO)_5$ | 2056, 2017 |
| $BrMn(CO)_5$ | 2064, 2017 |
| $ClMn(CO)_5$ | 2070, 2016 |

TABLE V

Iodo-pentacarbonylmanganese (XXXIII, X = I) in which the carbonyl groups possess more double bond character, absorbs at a lower frequency than the more polar chloro derivative (XXXIII, X = Cl)

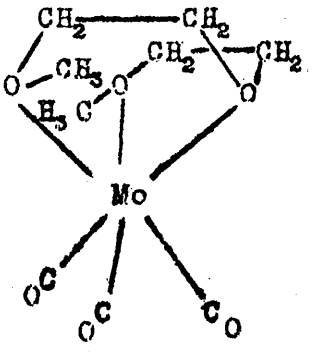
It was found that the iodo derivative (XXXIII, X = I) reacted with phenylisocyanide to give iodo-carbonyltetrakis (phenylisocyanide)manganese (XLI). The penta-substituted derivative was not observed in contrast to the reaction of the bromo derivative.

Chloro-pentacarbonylmanganese (XXXIII, X = Cl) underwent complete substitution by phenylisocyanide to give hexakis (phenylisocyanide)manganese chloride (XLIII). Conductance measurements show this compound to be a 1,1-electrolyte. The corresponding hexakis(phenylisocyanide)manganese iodide (XXXV) has been prepared from the $Mn^{++}$ salt according to the following equation:[92]

$$2MnI_2 + 12C_6H_5NC \longrightarrow Mn(CNC_6H_5)_6I + Mn(CNC_6H_5)_6I_3$$

As none of the lower substituted derivatives of bromo-pentacarbonylmanganese were found, alternative routes to such complexes were sought.

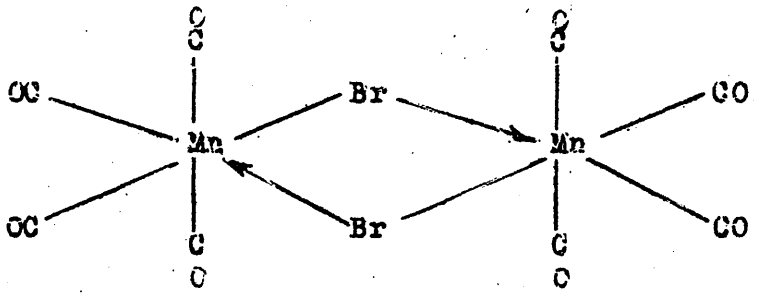
Molybdenum hexacarbonyl has been shown[98] to form tri-substituted derivatives <u>via</u> an intermediate etherate (XLIV) of diethylene glycol dimethyl ether (diglyme).




XLIV

Phenylisocyanide and bromo-pentacarbonylmanganese were found to react in the presence of warm diglyme to give bromo-dicarbonyltris(phenylisocyanide)manganese (XLV). That this reaction proceeds *via* a similar diglyme complex is supported by the evidence that a volume of gas equivalent to the displacement of three molecules of carbon monoxide is evolved when the halo-carbonyl is heated in diglyme.

Wilkinson *et al* has reported[97] the synthesis of bis(bromo-tetracarbonylmanganese) (XLVI), and assigned a structure in which there are two bridging halogen atoms bonded to the manganese atoms.




XLVI

Substitution reactions of compound (XLVI) are reported[97] to yield the disubstituted derivatives (XXXVII; X = Br) of bromo-pentacarbonylmanganese when carried out in refluxing ethanol. It was found however that at room temperature phenylisocyanide reacted with the dimer (XLVI) to give bromo-tetracarbonylphenyl-

isocyanidemanganese(XLVII). This illustration of the ease with which the halogen dative bond is broken is in agreement with the reactions of several other dimeric compounds containing similarily bonded halogen atoms. e.g. bis-chloro(ethylene)-uu'-dichlorodiplatinum[99], bis(dimethylaluminium chloride)[100].

Formation of substituted derivatives of halo-penta-carbonylmanganese suggested possible routes to substituted derivatives of dimanganese decacarbonyl. Bromo-pentacarbonyl-manganese has been shown to react with a variety of sodium salts of metal carbonyls to give the corresponding mixed metal derivatives.[101] However attempted reaction of the pentakis (XL), tetrakis (XXXIX), and bis (XXXVII, L = $C_6H_5NC$; X = Br) isocyanide derivatives of the bromo-carbonyl with a variety of reagents; metallic silver, zinc dust, cyclopentadienyl sodium, sodium borohydride, and sodium amalgam gave either unreacted starting material or gums which could not be obtained sufficiently pure for analysis.

The results of the above substitution reactions of halo-pentacarbonylmanganese by phenylisocyanide are summarised in Table VI.

It can be seen that the complete stepwise substitution of the bromo compound has been accomplished. Comparison with the products from similar reactions of the iodo and bromo derivatives confirms the conclusions which have been made from

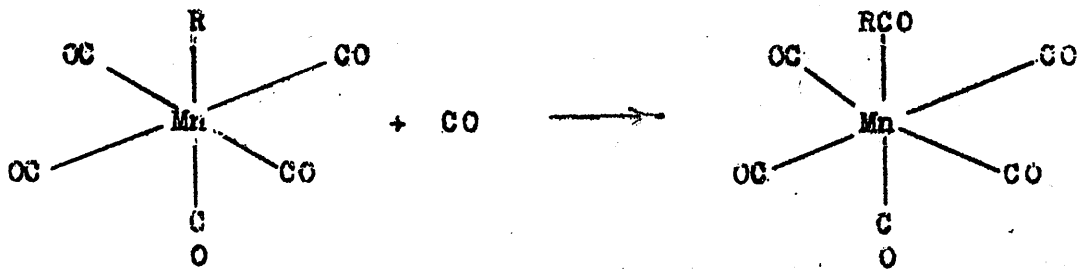
the exchange reactions regarding the effect of the halogen on the strength of the metal carbonyl bonds.

| Carbonyl Halide | Reaction Solvent | Reaction Temp. | Phenylisocyanide Substitution Derivatives. |
|---|---|---|---|
| $ClMn(CO)_5$ | T.H.F. | Reflux | $Mn(CNPh)_6Cl$ |
| $[BrMn(CO)_4]_2$ | T.H.F. | R/T | $BrMn(CO)_4(CNPh)$ |
| $BrMn(CO)_5$ | $C_2H_5OH$ | Reflux | $BrMn(CO)_3(CNPh)_2$ |
| $BrMn(CO)_5$ | Diglyme | 100°C | $BrMn(CO)_2(CNPh)_3$ |
| $BrMn(CO)_5$ | T.H.F. | Reflux | $BrMn(CO)(CNPh)_4$<br>$BrMn(CNPh)_5$ |
| $IMn(CO)_5$ | T.H.F. | Reflux | $IMn(CO)(CNPh)_4$ |

TABLE VI

The reactions of phenylisocyanide and methylpentacarbonylmanganese (XLVIII; R = $CH_3$) and phenylpentacarbonylmanganese (XLVIII; R = $C_6H_5$) have also been examined.

Compounds (XLVIII; R = $CH_3$) and (XLVIII; R = $C_6H_5$) have been shown[107] to react with carbon monoxide to give the corresponding acetyl (XLIX; R = $CH_3$) and benzoyl (XLIX; R = $C_6H_5$) derivatives. It has been shown[102] that the entering carbon monoxide group does not become attached to the alkyl or aryl group.

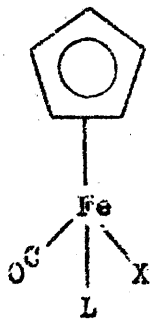



XLVIII XLIX

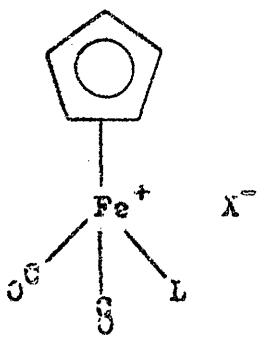
Amines have also been shown[103] to react with the methyl complex (XLVIII, R = $CH_3$) in a similar fashion to give the substituted acetyl derivative. By analogy it was expected that phenylisocyanide would also give addition compounds. However the products from this reaction were shown to be the dimeric derivatives; nonacarbonylphenylisocyanidedimanganese (L) and octacarbonylbis(phenylisocyanide)dimanganese (LI).

Isocyanide Derivatives of Cyclopentadienylmetal Carbonyl Halides.

As a result of the findings from the isocyanide substitution reactions of manganese carbonyl halides it was decided to investigate similar reactions of the cyclopentadienylmetal carbonyl halides of iron and molybdenum.




LII



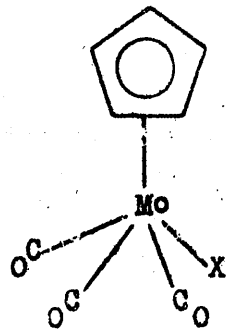

LIII

Chloro-dicarbonylcyclopentadienyliron (LII, L = CO; X = Cl) has been shown[104] to give the ionic derivative (LIII, L = CO; X = Cl) on treatment with carbon monoxide. Treatment of the chloro-derivative with triphenylphosphine also gives rise to the ionic derivative, dicarbonyltriphenylphosphine-cyclopentadienyliron chloride (LIII, L = $PPh_3$; X = Cl). It was found however that reaction of compound (LII, L = CO; X = Cl) with phenylisocyanide gave the completely substituted ionic complex; tris(phenylisocyanide)cyclopentadienyliron chloride (LIV). The higher substitution of compound

(LII, L = CO, X = Cl) with isocyanide may be attributed to the greater donor-acceptor properties of this ligand in contrast to the phosphine ligand.

The bromo-derivative (LII, L = CO; X = Br) was found to react with phenylisocyanide to give the covalent compound; bromo-bis(phenylisocyanide) cyclopentadienyliron (LV). Iodo-dicarbonylcyclopentadienyliron (LII, L = CO, X = I) was found to undergo substitution by phenylisocyanide to give a mixture of the two covalent derivatives; iodo-bis(phenylisocyanide)cyclopentadienyliron (LVI) and iodo-carbonylphenylisocyanidecyclopentadienyliron (LII, L = PhNC, X = I), the latter being the major product. This is in contrast to the reaction of the iodo derivative (LII; L = CO; X = I) with triphenylphosphine where the two products obtained are the addition complex (LIII; L = $PPh_3$ ;: X = I) and the mono-substituted derivative[101] (LII; L = $PPh_3$ ; X = I).

Similar results were obtained in the molybdenum series. Phenylisocyanide replaced three molecules of carbon monoxide from chloro-tricarbonylcyclopentadienylmolybdenum (XX; X = Cl) to give chloro-tris(phenylisocyanide)cyclopenta-dienylmolybdenum (LVII), whereas iodo-tricarbonylcyclopenta-dienylmolybdenum (XX, X = I) only underwent replacement of one




XX

carbonyl group on reaction with phenylisocyanide to give iodo-dicarbonylphenylisocyanidecyclopentadienyl molybdenum (LVIII)

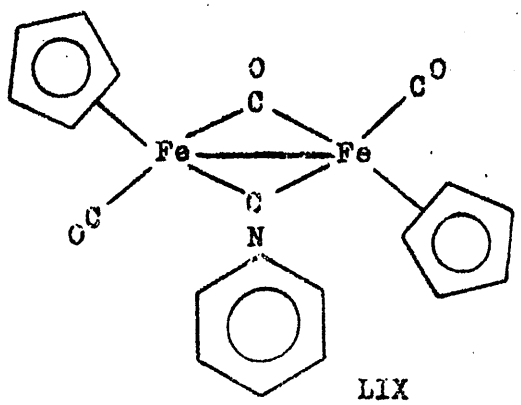
The above substitution reactions show that the cyclopentadienyl metal carbonyl halides behave in an analogous manner in substitution reactions to the manganese carbonyl halides, i.e. a decrease in the positive charge on the metal due to polarizability of the halogen results in an increase in the metal carbonyl bonds. Wojcicki and Basolo have obtained similar results from their exchange reaction studies in the cyclopentadienyliron carbonyl halide series.[89]

The mono substituted iron derivative (LII, L = $C_6H_5NC$, X = I) was also obtained from the reaction of the phosphine complex (LII, L = $PPh_3$; X = I) with isocyanide. The reverse process viz., replacement of isocyanide from compound (LII; L = $C_6H_5NC$; X = I) by phosphine failed to occur. Isocyanide was also found to displace phosphine from bromo-tricarbonylbis-(triphenylphosphine)manganese [XXXVII; L = $PPh_3$; X = Br]

to give the tetrakisisocyanide derivative (XXXIX). These reactions show that the phosphine ligand is more readily replaced than carbon monoxide or isocyanide from such mixed complexes.

Reaction of the phosphine complex (LII, L = $PPh_3$; X = I) with sodium borohydride has been reported[101] to lead to the stable hydride (LII, L = $PPh_3$; X = H). The stability of this complex is in contrast to the instability of the unsubstituted hydride (LII; L = CO, X = H) which readily decomposes to give the dimeric carbonyl derivative (XIX) and hydrogen[104]. It was found that treatment of the monoisocyanide derivative (LII; L = PhNC; X = I) with sodium borohydride under similar conditions gave rise to several products. Together with ferrocene (XI, M = Fe) and di(carbonyl-μ-carbonyl-cyclopentadienyliron) (XIX), there was isolated a red crystalline complex which analysed correctly for $(C_5H_5)_2Fe_2(CO)_3(CNC_6H_5)$. The infrared spectrum of this complex showed absorption in the terminal carbonyl stretching frequency region at 2004 $cm.^{-1}$ and 1949 $cm.^{-1}$ and also strong absorption at 1795 $cm.^{-1}$ and 1704 $cm.^{-1}$. The band at 1795 $cm.^{-1}$ has been assigned as due to the presence of a bridging carbonyl group by analogy with several other metal complexes containing bridging carbonyl groups. The peak at 1704 $cm.^{-1}$ is thought to be consistent with the presence of a bridging isocyanide group. Consequently structure (LIX) has

been assigned to this compound




LIX

By analogy with the unsubstituted dimer the isocyanide complex (LIX) should possess a structure with the carbonyl group and the isocyanide in the same plane. X-ray measurements, which are currently being recorded, should provide definite proof of such a structure. It has long been thought that isocyanide,[2] might behave in a similar fashion to carbon monoxide with respect to its ability to form bridging groups with transition metals. This complex is the first however to be reported containing a bridging isocyanide group.

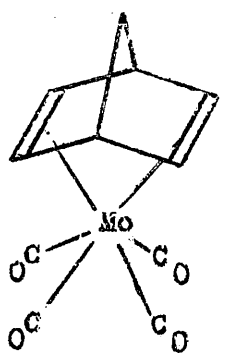
Alternative routes to this derivative were sought by reaction of the monosubstituted halide (LII, L = $C_6H_5NC$; X = I) with sodio-dicarbonylcyclopentadienyliron (LII, L=CO; X=Na) and the attempted substitution of the dimer (XIX) with isocyanide. The former reaction gave unchanged iodo-complex and the dimer, and in the latter reaction the dimer was recovered unchanged.

This result was not unexpected in view of the stability of the dimer e.g. it may be crystallised from boiling pyridine.

An attempt to dimerise iodo-bis(phenylisocyanide) cyclopentadienyliron (LVI) with sodium borohydride gave ferrocene as the major product and also very small quantities of gums which could not be identified.

Isocyanide substitution reactions of carbonyl derivatives of chromium and molybdenum.

Bicyclo[2:2:1]hepta-2,5-diene (norbornadiene) has been shown[103] to react with molybdenum carbonyl to give complex (LX). It was found that reaction of this complex with




LX

phenylisocyanide led to displacement of the hydrocarbon residue by isocyanide to give tetracarbonylbis(phenylisocyanide) molybdenum (LXI).

An attempted substitution reaction of dicarbonyl tropyliummolybdenum iodide (LXII) with phenylisocyanide led only to decomposition of the starting material.

A series of reactions was attempted designed to synthesise the isocyanide analogue of tricarbonylbenzene chromium (XXV). Direct reaction of complex (XXV) and phenylisocyanide resulted in unchanged starting material. Phenylisocyanide was found to react readily with tricarbonyl-cycloheptatrienechromium (LXIII) displacing the hydrocarbon residue to give tricarbonyltris(phenylisocyanide)chromium (LXIV). Several other isocyanides have been found[106] to react in this fashion with compound (LXIII).

No reaction was observed on heating the mixed carbonyl isocyanide derivative (LXIV) in refluxing 1,3,5-trimethylbenzene in contrast to the reaction of the unsubstituted carbonyl which gives tricarbonyl 1,3,5-trimethylbenzene (LXV) chromium.

Displacement of isocyanide from hexakis(phenyliso-cyanide)chromium (LXVI) by cyclohepta-1,3,5-triene was found to be equally difficult and no reaction occurred even on raising the reaction temperature to 165°C.

Isocyanide substitution reactions of Cobalt and Nickel derivatives.

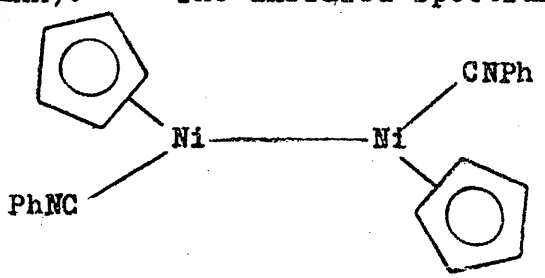
An unsuccessful attempt was made to synthesise the isocyanide analogue of dicarbonylcyclopentadienylcobalt (XIV) by the reaction of pentakis(phenylisocyanide)cobalt iodide (LXVII) with cyclopentadienyl sodium. Extensive decomposition occurred and the presence of a metal isocyanide complex was not observed.

The preparation of $(CO)_5$ Mn-Co$(CO)_4$ (LXXXIV) has recently been reported.[108] An attempt was made to prepare an isocyanide derivative by reaction of the cobalt complex (LXVII) with sodio-pentacarbonylmanganese. The major product from this reaction was manganese carbonyl. A brown gum was also obtained which showed characteristic absorption peaks in the infrared of isocyanide and carbonyl groups. Attempts to purify this product proved unsuccessful.

An unsuccessful substitution reaction was observed when sodio-tetracarbonylcobalt and phenylisocyanide were heated at 65°C. Treatment of the reaction mixture with iodomethane and chromatography did not yield any metal isocyanide derivative.

Reaction of bis(μ-carbonyl-carbonylbicyclo-[2,2,1]-hepta-2,5-dienecobalt) (LXVIII) with phenylisocyanide caused decomposition of the starting material and did not yield any stable isocyanide complex.

The labile nature of the cyclopentadienyl groups in dicyclopentadienylnickel (XI, M = Ni) is shown by the reaction of this complex with phenylisocyanide. Reaction occurs readily at room temperature to give tetrakis(phenylisocyanide)nickel (LXIX). Nickel tetracarbonyl has been shown[39] to undergo reaction with dicyclopentadienylnickel to give the dimeric carbonyl complex. Reaction of the nickel isocyanide derivative with dicyclopentadienylnickel gives a similar type of complex, di(phenylisocyanidecyclopentadienylnickel) (LXX). The infrared spectrum of this complex shows




LXX

only one absorption peak at 2174 $cm.^{-1}$. This suggests that the isocyanide groups are not bridging and structure (LXX) has tentatively been assigned to this derivative. An X-ray analysis of this compound is in progress.

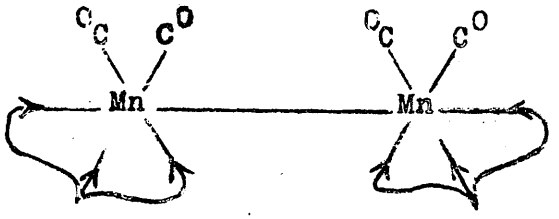
# THEORETICAL

## PART II

## HETEROCYCLIC METAL CARBONYLS

During the course of their investigations into the occurrence of bridging carbon monoxide groups, as evidenced by their absorption in the carbonyl stretching region of the infrared, Joshi and Pauson investigated the possibility of preparing a dimeric manganese carbonyl derivative containing two such bridging groups.

It was thought that the substitution of manganese carbonyl by arene systems might give rise to a di-arene metal carbonyl complex (LXXI) in which the carbonyl groups may be in a favourable position to allow bridging to occur, assuming that the dimeric molecule retained a near octahedral configuration after substitution.

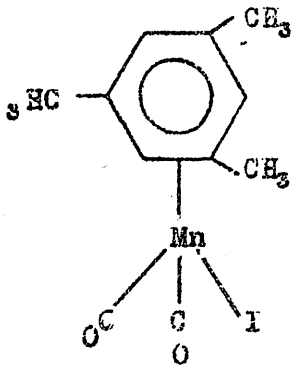



LXXI

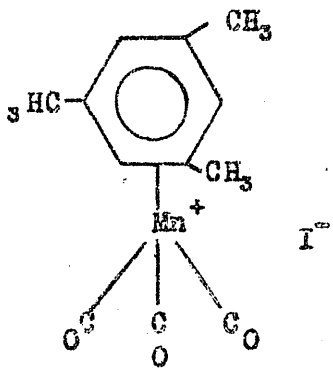
Substitution of manganese carbonyl by several ligands has been reported to give disubstituted dimers of the type, $(CO)_5Mn\text{-}Mn(CO)_3L_2$.[111,112] Although benzene does not appear to react with manganese carbonyl, mesitylene has been reported in a patent[113] to react to give bis(dicarbonylmesitylenemanganese

(LXXII). This compound has not been fully characterised and the preparation could not be repeated using the few experimental details provided.

An alternative route to complex (LXXI) appeared possible by dimerisation of the monomer, iodo-dicarbonylmesitylenemanganese (LXXIII). An attempt was made to synthesise compound (LXXIII) from the ionic complex, tricarbonylmesitylenemanganese iodide (LXXIV) which is readily formed from the hydrocarbon and halo-pentacarbonylmanganese under Friedel-Crafts conditions.[114]




LXXIII




LXXIV

Reaction of dicarbonyltriphenylphosphinecyclopentadienyliron iodide (LII, L = $PPh_3$ X = I) with trityl chloride in the presence of zinc gives di(carbonyl-μ-carbonylcyclopentadienyliron) (XIX) and the covalent complex iodo-carbonyltriphenylphosphinecyclopentadienyliron (LII, L = $PPh_3$, X = I)[101]. A similar reaction with complex (LXXIV) gave only small yields of the monomer (LXXIII) and no dimeric derivatives.

A further route to the dimeric derivative (LXXI) was next attempted using pyrrole and manganese carbonyl. Pyrrole, $C_4H_5N$, is unique in the sense that it could react with metal carbonyls in the following fashions:

(i) Interaction of the lone pair on the nitrogen atom with metal carbonyls to give substitution type complexes similar to those formed by pyridine and metal carbonyls, e.g. $Mo(CO)_5(C_5H_5N)$.[116] This type of reaction is unlikely in view of the extremely low basicity of pyrrole.[115]

(ii) Interaction of the conjugated diene system with metal carbonyls similar to the reactions of 1,3-butadiene, 1,3-cyclohexadiene, etc.[117-120]

(iii) Combination of effects (i) and (ii) to behave formally as a cyclic triene system e.g. thiophene in tricarbonylthiophene-chromium.

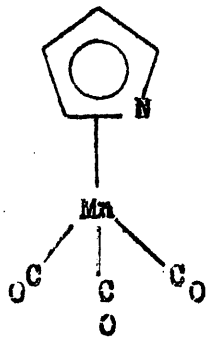
(iv) Replacement of the hydrogen atom attached to the nitrogen atom by a metal carbonyl residue to give a sigma-bonded complex similar to the $\sigma$-cyclopentadienyl ring in dicarbonyl-$\sigma$-cyclopentadienyl-$\pi$-cyclopentadienyliron.

(v) Substitution in the $\alpha$ or $\beta$ position of the pyrrole ring by a metal carbonyl residue.

(vi) Combination of effects (ii) and (iv) to give a complex in which the bonding of the pyrrole to the metal is similar to

that in $\pi$-cyclopentadienyl complexes of transition metals.

The yellow crystalline material obtained from the reaction of pyrrole and manganese carbonyl in refluxing ethylene glycol diethyl ether analysed correctly for a compound of empirical formula, $C_7H_4MnNO_3$. Detailed examination of this complex by infrared, ultraviolet and nuclear magnetic resonance techniques led to the assignment[121] of structure (LXXV) in which the heterocycle is bonded to the metal in an analogous fashion to the bonding of the cyclopentadienyl ring in tricarbonylcyclopentadienylmanganese.




LXXV

As a result of this work by Joshi and Pauson it was decided to investigate the possible existence of other complexes containing heterocycles bonded to a transition metal in this fashion.

The reaction of pyrrole and manganese carbonyl was repeated in 100/120 ligroin to give a slightly increased yield of complex (LXXV). Thus the choice of reaction solvent appears to be of little significance.

The reactions of various substituted pyrroles were investigated. 2-Methylpyrrole was found to react with manganese carbonyl to give tricarbonyl-2-methylpyrrolylmanganese (LXXVI). This compound is a pale yellow liquid which decomposes on exposure to air. Reaction of pyrrole-2-aldehyde with manganese carbonyl resulted in extensive decomposition. This may be due to the inductive effect of the aldehyde group which reduces the stability of the desired complex, tricarbonyl-[pyrrolyl-2-aldehyde]-manganese, and also to the loss of symmetry.

That the latter effect is a factor in determining the relative stability of these complexes is illustrated by the instability of complex (LXXVI) which decomposes on exposure to air. The more symmetrical tricarbonyl-2,5-dimethylpyrrolyl-manganese (LXXVII), which has subsequently been synthesised in these laboratories, and the unsubstituted complex (LXXV) appear to be more stable.

A reaction was next attempted between N-methylpyrrole and manganese carbonyl to investigate the possible formation of bis(tricarbonyl-N-methylpyrrolemanganese), bis(dicarbonyl-N-methylpyrrolemanganese) or the charged complex, tricarbonyl-N-

methylpyrrolylmanganese. No reaction occurred however and the manganese carbonyl was recovered unchanged.

As the chemistry of $\pi$-cyclopentadienyl complexes is extensive it was decided to investigate the possible existence of $\pi$-pyrrolyl complexes of other transition metals.

Cyclopentadiene has been shown to react with the carbonyls of Groups VI metals to give bis(tricarbonylcyclopentadienylmetal) complexes. Reaction of pyrrole with molybdenum carbonyl gave a yellow solution which rapidly decomposed on exposure to air and proved too unstable to handle. Since the reaction medium used was diglyme it seems not unreasonable to assume the formation of the diglyme metal carbonyl complex (XLIV)[98] which decomposed on exposure to air.

The synthesis of $\pi$-cyclopentadienyl metal complexes has been facilited by the ready formation of the alkali salts of cyclopentadiene. Pyrrole also reacts with potassium to give pyrrolyl potassium, $C_4H_4N^-K^+$. The only reported reaction of pyrrolyl potassium with a transition metal halide with a view to preparing $\pi$-bonded complexes analogous to $\pi$-cyclopenadienyl metal derivatives is by Fischer and Ofele.[64] They did not observe any reaction between pyrrolyl potassium and hexamminonickel(II) thiocyanate.

It was found that pyrrolyl potassium on reaction with both bis(triphenylphosphine)nitrosyl nickel bromide and bis (triphenylphosphine)nickel bromide caused decomposition. The only product obtained being triphenylphosphine.

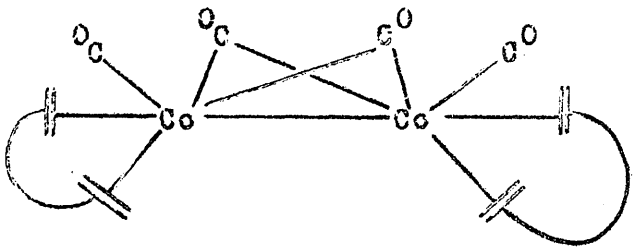
The reaction of pyrrolyl potassium with bromo-pentacarbonylmanganese (XXXIII, X = Br) in refluxing tetrahydrofuran however gave complex (LXXV). It is likely that this reaction proceeds via the $\sigma$-bonded intermediate, pentacarbonyl-pyrrolemanganese which under the conditions employed lost two molecules of carbon monoxide to give the $\pi$-bonded tricarbonyl derivative.

Unsuccessful attempts were made to expand this reaction to indole. Both the reactions of indolyl potassium with bromo-pentacarbonylmanganese and indole with manganese carbonyl gave only starting materials. The presence of small quantities of any products proved difficult to detect due to the difficulty of removing unreacted indole.

The hydrides of tricarbonylcyclopentadienyltungsten and molybdenum have been prepared[124] by treatment of the sodium salt from the reaction of the metal carbonyl and cyclopentadienyl sodium, with acetic acid. A similar reaction was attempted with molybdenum carbonyl and pyrrolyl potassium. The reaction mixture turned yellow on addition of the pyrrolyl salt

to the metal carbonyl. Treatment of the reaction mixture with acetic acid and carbon tetrachloride gave only molybdenum carbonyl, suggesting that either the intermediate hydride and/or the chloride are too unstable to isolate.

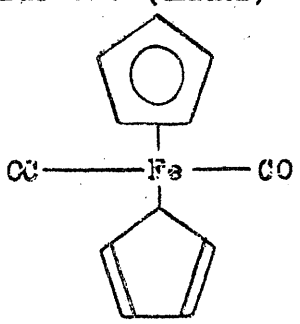
The reaction of bis(tetracarbonylcobalt)mercury (LXXVIII) with bicyclo-[2,2,1]-hepta-2,5-diene has been shown[122] to give the substituted dimeric complex (LXXIX). No reaction was observed when complex (LXXVIII) and pyrrole were heated together.




LXXIX

[123]

Hallam and Pauson have reported that bromo-dicarbonyl-cyclopentadienyliron (LII; L = CO; X = Br) undergoes reaction with cyclopentadienylsodium to give a complex $(C_5H_5)_2Fe(CO)_2$ (LXXX) to which structure (LXXXI) has been assigned.




LXXXI

A similar reaction of iodo-dicarbonylcyclopentadienyl-iron with pyrrolyl potassium as well as giving ferrocene also gave a small yield of a red crystalline compound which analysed correctly for $(C_5H_5)(C_4H_4N)Fe$. Structure (LXXXII) has been assigned to this complex on the basis of the strong "9,10" bands in the infrared spectrum and the similarity to ferrocene of its ultraviolet spectrum.


LXXXII

The nuclear magnetic resonance spectrum of this compound shows three peaks at 4.72$\tau$, 5.55$\tau$, and 5.85$\tau$. The former may be assigned to the $\alpha$ and $\beta$ protons on the heterocyclic ring. The latter peak has been assigned to the protons of the cyclopentadienyl ring. The orientation of the rings with respect to each other awaits the X-ray analysis.

No complexes were isolated from this reaction corresponding to types (iv) and (v) suggested earlier. In the separation of the reaction products by chromatography it was

noticed that complex (LXXXII) was eluted by ether unlike ferrocene which is readily eluted by ligroin. This increase in polarity in substituting a $\pi$-cyclopentadienyl group by a $\pi$-pyrrolyl group was also observed in the purification of tricarbonylpyrrolylmanganese which was eluted by ligroin/benzene whilst tricarbonylcyclopentadienylmanganese is readily eluted by ligroin.

A logical extension of the preparation of compound (LXXXII) appeared to be the reaction of iodo-tetracarbonyliron, $Fe(CO)_4I_2$ (LXXXIII) with pyrrolyl potassium to give the pyrrole analogue of ferrocene. Complex (LXXXIII) has been shown[123] to react with cyclopentadienyl sodium to give ferrocene.

However addition of the pyrrolyl salt to a tetrahydrofuran suspension of complex (LXXXIII) caused complete decomposition.

An attempt was made using the iodide, $(C_5H_5)Fe(CO)_2I$, and the potassium salt of carbazole to prepare the carbazole analogue of compound (LXXXII). Decomposition occurred however, which may have been due to the instability of the desired complex. In the analogous homocyclic series the cyclopentadienyl complex is more stable than the indenyl derivative whilst the fluorene compound has not been isolated.

# EXPERIMENTAL

## PART I

General.

All reactions were carried out in an atmosphere of oxygen-free ("white-spot") nitrogen.

Spence's 'Grade H' alumina was used for chromatography and was partially deactivated by exposure to the atmosphere for 3 hr.

Neutralized alumina was prepared by storing 'Grade H' alumina over ethyl acetate for 1-2 days, filtering, washing with methanol and water and finally drying at 160°C, for 4 hr.

Molecular weights were determined cryoscopically in benzene solution.

All melting points are uncorrected and were determined in sealed, evacuated capillary tubes.

Unless otherwise stated, all infrared spectra were recorded as potassium chloride discs.

Petrol or ligroin refers to that fraction of petroleum ether of b.p. 60-80°C.

Tris(phenylisocyanide)cyclopentadienylmanganese. - A solution of hexakis(phenylisocyanide)manganese iodide[92] (4 g., 5 mmole) in N,N-dimethylformamide (50 ml.) was added to a solution of cyclopentadienyl sodium, prepared from sodium (0.34 g., 0.015 g. atom) and excess cyclopentadiene, in tetrahydrofuran (15 ml.). The mixture was stirred for 17 hr. at room temperature. Methyl alcohol (5 ml.) was added and the mixture was stirred for a further 15 min. after which the solvent was removed in vacuo. The residue was extracted with a minimum quantity of benzene and chromatographed on neutral alumina. Ligroin eluted trace amounts of phenylisocyanide. Ligroin benzene (1:1) eluted a yellow band which afforded yellow needles (0.36 g., 20%) m.p. 97°C., which were recrystallised from chilled pentane. Tris(phenylisocyanide)cyclopentadienylmanganese shows intense absorption in the metal isocyanide stretching frequency region of the infrared at 2096 cm.$^{-1}$ and 1961 cm.$^{-1}$ ($CCl_4$).

| | | |
|---|---|---|
| | Found: | C,72.7; H,4.4; N,9.8. |
| $C_{26}H_{20}MnN_3$ | requires | C,72.7; H,4.7; N,9.8% |

Reaction of bromo-pentacarbonylmanganese with excess phenylisocyanide. - Phenylisocyanide[127] (5.15 g., 0.05 mole) and bromo-pentacarbonylmanganese[87] (2.75 g., 0.01 mole) were stirred in refluxing tetrahydrofuran (100 ml.) for 6 hr. The

mixture was cooled and the solvent removed *in vacuo*. The residue (5.9 g.) was extracted with warm benzene ((3 x 20 ml.) leaving a pale yellow solid (0.4 g., 0.61 mmole) which crystallised from tetrahydrofuran as colourless plates, m.p. 213°C (dec.). Bromo-pentakis(phenylisocyanide)manganese shows maxima in the metal isocyanide stretching frequency region of the infrared at 2101 $cm.^{-1}$ (strong) and 2012 $cm.^{-1}$ (medium) ($C_2H_4Cl_2$)

Found: C,64.9; H,4.3; Br,12.5; N,11.0;

$C_{35}H_{25}BrMnN_5$ requires: C,64.6; H,3.9; Br,12.2; N,10.8%

The benzene extract was evaporated to dryness *in vacuo* and the residue (2.3 g., 4 mmole) crystallised from tetrahydrofuran as orange crystals, m.p. 180°C (dec.). The infrared absorption of bromo-carbonyltetrakis(phenylisocyanide)manganese shows maxima at 2101 $cm.^{-1}$ (very strong), 2012 $cm.^{-1}$ (medium) and 1919 $cm.^{-1}$ (strong) ($CCl_4$)

Found: C,61.2; H,4.0; Br,14.0; N,9.7; O,3.1; M,567

$C_{29}H_{20}BrMnN_4O$ requires: C,60.5; H,3.5; Br,13.9; N,9.7; O,2.8% M,575.

Bromo-dicarbonyltris(phenylisocyanide)manganese.- Phenylisocyanide (1.54 g., 15 mmole) was added to a solution of bromo-pentacarbonylmanganese (1.37 g., 5 mmole) in diethylene glycol dimethyl ether (50 ml.), and the mixture stirred at 100°C for 3 hr. Cooling and removal of the solvent *in vacuo* left a

solid which was recrystallised from diethyl ether to yield yellow crystals of bromo-dicarbonyltris(phenylisocyanide) manganese, m.p. 129-130°C(1.58 g., 65%).

Infrared absorption maxima occurred at 2179 cm.$^{-1}$ (weak) 2114 cm.$^{-1}$ (strong), 2049 cm.$^{-1}$ (strong), 2020 cm.$^{-1}$ (strong) and 1942 cm.$^{-1}$ (strong).

Found: C,55.4; H,3.0; N,8.7;

$C_{23}H_{15}BrMnN_3O_2$ requires: C,55.2; H,3.0; N,8.4%

Bromo-tricarbonylbis(phenylisocyanide)manganese.- Phenylisocyanide (2.06 g., 0.02 mole) was added to a solution of bromo-pentacarbonylmanganese (2.75 g., 0.01 mole) in absolute alcohol (60 ml.). The mixture was stirred at 60°C for 3 hr. After cooling, the solvent was removed in vacuo to give a yellow solid which crystallised from methylene chloride/ligroin as pale yellow needles, m.p. 84-86°C (3.05 g., 70%). Bromo-tricarbonylbis(phenylisocyanide)manganese shows maxima in the infrared at 2198 cm.$^{-1}$ (medium), 2174 cm.$^{-1}$, 2053 cm.$^{-1}$ 2004 cm.$^{-1}$ 1954 cm.$^{-1}$ (all strong):

Found: C,48.7; H,2.4; N,7.0;

$C_{24}H_{15}BrMnN_2O_3$ requires: C,48.0; H,2.4; N,6.6%

Bromo-tetracarbonylphenylisocyanidemanganese. - Phenylisocyanide (0.8 g., 8 mmole) was added to a solution bis(bromo-tetracarbonylmanganese)[87] (0.429 g., 0.87 mmole) in

tetrahydrofuran (50 ml.) and the mixture stirred at room temperature for 4 hr. The solvent was removed *in vacuo* and the residue crystallised from metylene chloride/ligroin to give yellow needles, m.p. 86-87°C (140 mg., 45%). *Bromo-tetracarbonylphenylisocyanidemanganese* absorbs in the infrared at 2188 $cm.^{-1}$ (weak) 2107 $cm.^{-1}$ (weak) 2045 $cm.^{-1}$ (strong) and 1993 $cm.^{-1}$ (medium) ($CCl_4$)

Found: C,37.4; H,1.8; N,4.2;

$C_{11}H_5BrMnNO_4$ requires: C,37.7; H,1.4; N,4.0%

*Reaction of bromo-pentacarbonylmanganese with tetrahydrofuran and diglyme.* - Bromo-pentacarbonylmanganese (2.75 g., 0.01 mole) was heated in tetrahydrofuran (50 ml.) at reflux for 4 hr and the volume of gas evolved was found to be 420 ml. The theoretical volume equivalent to displacement of 4 molecules of carbon monoxide is 448 ml.

A similar reaction carried out in diglyme caused evolution of 300 ml. of gas. The volume equivalent to displacement of three molecules of carbon monoxide is 336 ml.

*Iodo-carbonyl tetrakis(phenylisocyanide)manganese.* - Iodo-pentacarbonylmanganese[126] (0.5 g., 1.5 mmole) and phenylisocyanide (1.0 g., 0.01 mole) were stirred in refluxing tetrahydrofuran (30 ml.) for 3 hr. The mixture was cooled and the solvent removed *in vacuo*. The residue crystallised from diethyl ether as yellow crystals, m.p. 171°C (0.47 g., 51%).

Iodo-carbonyl tetrakis(phenylisocyanide)manganese shows maxima in the infrared at 2088 cm.$^{-1}$ (strong), 1992 cm.$^{-1}$ (medium) and 1894 cm.$^{-1}$ (strong)

Found: C,55.6; H,3.3; N,9.2;

$C_{29}H_{20}IMnN_4O$ requires: C,55.9; H,3.3; N,9.0%.

Hexakis(phenylisocyanide)manganese chloride. - Phenylisocyanide (5.15 g., 0.05 mole) and chloro-pentacarbonyl-manganese (2.3 g., 0.01 mole) were stirred in refluxing tetra-hydrofuran (50 ml.) for 4 hr. The mixture was cooled and the solvent removed in vacuo. The residual brown gum crystallised from methylene chloride/ligroin as pale yellow crystals, m.p. 178°C (2.3 g., 32%). Hexakis(phenylisocyanide)manganese chloride absorbs in the metal isocyanide stretching frequency region of the infrared at 2114 cm.$^{-1}$ (very strong) and 2016 cm.$^{-1}$ (strong)

Found: C,70.7; H,4.5; N,11.8;

$C_{42}H_{30}ClMnN_6$ requires: C,71.1; H,4.3; N,11.8%.

Conductivity (nitrobenzene, 25°C)

$\alpha\ Mn(CNC_6H_5)_6Cl = 28.4\ \Omega^{-1}$

$\alpha\ Mn(CNC_6H_5)_6I = 27\ \Omega^{-1}$

Substitution of methylpentacarbonylmanganese with phenylisocyanide. - A mixture of methylpentacarbonylmanganese[128] (2.1 g., 0.01 mole) and phenylisocyanide (1.8 g., 18 mmole) in tetrahydrofuran (40 ml.) were heated with stirring at reflux for 3 hr. After cooling the mixture, the solvent was removed in vacuo. The residue was dissolved in a minimum of benzene and

chromatographed. Elution with hexane gave four compounds. Unreacted phenylisocyanide was eluted first, followed by manganese carbonyl (15 mg.). The third band from the chromatogram afforded yellow crystals, m.p. 54°C, (132 mg. 5.6%) which were recrystallised from pentane. Nonacarbonylphenylisocyanidedimanganese shows intense absorption in the infrared at 2169 $cm.^{-1}$, 2101 $cm.^{-1}$, 2045 $cm.^{-1}$ 2016 $cm.^{-1}$ and 1980 $cm.^{-1}$ ($CCl_4$) (all strong).

Found: C,41.1; H,1.5; N,3.1

$C_{13}H_5Mn_2NO_9$ requires: C,41.3; H,1.1; N,3.0%

The final band eluted with hexane gave yellow crystals (112 mg. 4%) of bis(tetracarbonylphenylisocyanidemanganese), m.p. 111°C, which were recrystallised from pentane. Infrared absorption maxima occurred at 2165 $cm.^{-1}$ (weak) 2128 $cm.^{-1}$ (medium) 2062 $cm.^{-1}$ (medium), 2020 $cm.^{-1}$ (medium) 1996 $cm.^{-1}$ (strong) and 1957 $cm.^{-1}$ (medium) ($CCl_4$).

Found: C,49.1; H,2.6; N,5.2;

$C_{22}H_{10}Mn_2N_2O_8$ requires: C,48.9; H,1.9; N,5.2%.

Substitution of phenylpentacarbonylmanganese with phenylisocyanide. - Phenylisocyanide (1 g., 0.01 mole) and phenylpentacarbonylmanganese[128] (2.7 g., 0.01 mole) were stirred in refluxing tetrahydrofuran (60 ml.) for 2 hr. The mixture was cooled and the solvent removed in vacuo. The residue was dissolved in a minimum of benzene and chromatographed. The

products obtained, in order of elution by hexane, were; phenylisocyanide, phenylpentacarbonylmanganese, nonacarbonyl-phenylisocyanidedimanganese (0.14 g., 5%), and bis(tetracarbonyl-phenylisocyanidemanganese) (0.095 g., 3%). The products were identified by m.p. and infrared spectroscopy.

Attempted reaction of bromo-pentakis(phenylisocyanide) manganese with Zinc. - To a solution of bromo-pentakis(phenyl-isocyanide) (0.65 g., 1 mmole) in benzene (50 ml.) was added zinc dust (0.1 g.). The mixture was stirred at reflux for 14 hr. After cooling, the mixture was filtered and the solvent removed *in vacuo*. The residue was dissolved in benzene and chromatographed. Elution with benzene afforded an orange gum (42 mg.), the infrared spectrum of which showed the presence of isocyanide groups. The gum could not be obtained crystalline and was not examined further.

Attempted reaction of bromo-carbonyltetrakis(phenyl-isocyanide)-manganese with silver. - Powdered silver (4 g., 0.04 g. atom) was added to a solution of bromo-carbonyltetrakis-(phenylisocyanide)manganese (2.87 g., 5 mmole) in tetrahydrofuran (150 ml.). The mixture was stirred at room temperature for 72 hr. The mixture was filtered and the solvent removed *in vacuo*. The residue was extracted with methylene chloride and precipitated with ligroin to give starting material

(1.97 g., 69%).

Attempted reaction of bromo-carbonyltetrakis(phenylisocyanide)manganese with sodium borohydride. - Sodium borohydride (0.095 g.) and bromo-carbonyltetrakis(phenylisocyanide)manganese (1.15 g., 2 mmole) were heated in benzene (40 ml.) at reflux for 4 hr. After cooling, water (30 ml.) was added cautiously to the reaction mixture. The mixture was shaken and the water layer removed. Removal of the benzene in vacuo gave unchanged starting material (0.94 g., 82% rec.).

Attempted reaction of bromo-carbonyltetrakis(phenylisocmanganese with cyclopentadienyl sodium. - A solution of bromo-carbonyltetrakis(phenylisocyanide)manganese (4.3 g., 7.5 mmole) in tetrahydrofuran (50 ml.) was added to a solution in tetrahydrofuran (30 ml.) of cyclopentadienyl sodium (0.03 mole), prepared from sodium (0.69 g., 0.03 g. atom) and excess cyclopentadiene. The mixture was stirred at room temperature for 14 hr. After the removal of the solvent in vacuo, the residue was extracted with benzene (3 x 15 ml.) and chromatographed. Ligroin/benzene (1:1) eluted a yellow oil (340 mg.) which showed strong absorption in the metal isocyanide stretching frequency region of the infrared. Distillation in high vacuum caused complete decomposition. Benzene eluted a purple gum (210 mg.) and ether eluted a deep red gum (210 mg.). The absorption in the metal isocyanide

stretching frequency region of the infrared of both these complexes was extremely weak and they were not examined further.

Attempted reaction of bromo-carbonyltetrakis(phenylisocyanide)manganese with sodio-pentacarbonylmanganese. - Bromo-carbonyltetrakis(phenylisocyanide)manganese (1.9 g., 3 mmole) in solution in tetrahydrofuran (60 ml.) was added to a solution in tetrahydrofuran (20 ml.) of sodio-pentacarbonylmanganese, prepared from sodium (0.077 g., 3.5 mg. atom) and manganese carbonyl (0.65 g., 1.5 mmole). The mixture was stirred for 3 hr. at room temperature. The solvent was removed *in vacuo*. Extraction with ligroin gave manganese carbonyl (0.4 g., 61%) and left unreacted bromo-carbonyltetrakis(phenylisocyanide)manganese (1.73 g., 90%).

Attempted reaction of bromo-tricarbonylbis(phenylisocyanide)manganese with sodium amalgam. - Bromo-tricarbonylbis (phenylisocyanide)manganese (1.41 g., 3 mmole) in solution in tetrahydrofuran (30 ml.) was added to sodium amalgam (1%, 8 g. 0.003 g. atom of sodium) and the mixture stirred for 3 hr. at room temperature. Iodomethane (2.27 g., 0.016 mole) was then added, and the solution stirred for one hr. further at room temperature. The mixture was filtered and the solvent removed *in vacuo*. The residual brown gum (112 mg.) showed maxima in the infrared 2178 $cm.^{-1}$ (weak), 2123 $cm.^{-1}$ (strong) 2016 $cm.^{-1}$ (strong) and 1953 $cm.^{-1}$ (strong). It could not be obtained pure for analysis and was not examined further.

Reaction of bromo-tricarbonylbis(triphenylphosphine) manganese with phenylisocyanide. - Phenylisocyanide (1.03 g., 0.01 mole) was added to a solution of bromo-tricarbonylbis(triphenylphosphine)manganese[86] (1.83 g., 2.5 mmole) in tetrahydrofuran (50 ml.). The mixture was stirred at reflux for 3 hr. After cooling, the solvent was removed in vacuo and the residue recrystallised from tetrahydrofuran to give bromo-carbonyltetrakis (phenylisocyanide)manganese (0.63 g., 44%) which was identified by infrared evidence and m.p.

Substitution of iodo-dicarbonylcyclopentadienyliron with phenylisocyanide. - Iodo-dicarbonylcyclopentadienyliron[123] (18.2 g., 0.06 mole) and phenylisocyanide (9 g., 0.87 mole) in solution in benzene (150 ml.), were stirred at reflux for 6 hr. After cooling the solvent was removed in vacuo and the residue extracted with ether and chromatographed. Ligroin/benzene (10:1) eluted ferrocene (99mg., 10%) which was identified by m.p. and infrared spectrum. Ligroin/benzene (6:4) eluted two bands. The first was unchanged iodo-dicarbonylcyclopentadienyliron (9.72 g., 53%) and the second band afforded brown needles (8.5 g. 35%) m.p. 108°C after recrystallisation from methylene chloride/ligroin Iodo-carbonylphenylisocyanidecyclopentadienyliron shows two intense bands at 2151 $cm.^{-1}$ and 1969 $cm.^{-1}$ (KI) in the infrared, corresponding to the stretching frequencies of metal isocyanide and metal carbonyl respectively.

Found: C,41.7; H,2.8; N,3.8;

$C_{13}H_{10}FeINO$ requires: C,41.2; H,2.7; N,3.7%

Ligroin/benzene (1:3) eluted a maroon band which afforded deep red crystals (2.3 g. 8%) m.p. 104-105°C, which were recrystallised from methylene chloride/ligroin. Iodo-bis(phenylisocyanide)cyclopentadienyliron absor/ligroin 55 cm.$^{-1}$ (strong) and 2096 cm.$^{-1}$ (strong) 2024 (weak) (KI) in the infrared corresponding to the metal isocyanide stretching frequency

Found: C,50.0; H,3.7; N,5.5;

$C_{19}H_{15}FeIN_2$ requires: C,50.2; H,3.3; N,6.1%

The insoluble residue (1.6 g.) from the reaction showed absorption in the infrared in both the metal carbonyl and the metal isocyanide stretching frequency regions, and also showed "9,10" bands indicating the presence of a cyclopentadienyl ring The material could not be obtained crystalline and was probably a mixture of several ionic complexes.

Substitution of bromo-dicarbonylcyclopentadienyliron with phenylisocaynide. - Phenylisocyanide (1.01 g., 0.01 mole) was added to a solution of bromo-dicarbonylcyclopentadienyliron[123] (1.28g., 0.005 mole) in benzene (60 ml.), and the mixture stirred at reflux for 3 hr. After cooling, the solvent was removed in vacuo. The residue was extracted with a minimum of benzene and chromatographed. Ligroin/ether (9:1) eluted unreacted phenyliso-cyanide. Ligroin/ether (1:2) eluted a deep red band which

afforded purple needles (0.75 g., 37%), m.p. 107°C, after recrystallisation from methylene chloride/ligroin. Bromo-bis(phenylisocyanide)cyclopentadienyliron absorbs in the infrared at 2155 $cm.^{-1}$ (strong) 2087 $cm.^{-1}$ (strong) and 2020 $cm.^{-1}$ (weak) (KI) in the metal isocyanide stretching frequency region

Found, N,7.1

$C_{19}H_{18}FeN_2B$ requires, N,6.9%

Retained on the chromatogram was a red band which could not be eluted by acetone.

Reaction of chloro-dicarbonylcyclopentadienyliron with phenylisocyanide. - Phenylisocyanide (6.18 g., 60 mmole) was added to a solution of chloro-dicarbonylcyclopentadienyliron[123] (4.24 g., 20 mmole) in benzene (50 ml.), and the mixture stirred at reflux for 90 min. After cooling, the solvent was removed in vacuo. The residue (6.3 g., 68%) crystallised from methylene chloride/ligroin as orange needles, m.p. 174°C (dec.). Tris-(phenylisocyanide)cyclopentadienyliron chloride shows maxima in the infrared at 2190 $cm.^{-1}$ and 2123 $cm.^{-1}$ (both strong)

Found: C,67.0; H,4.5; N,9.1;

$C_{26}H_{20}ClFeN_3$ requires: C,67.0; H,4.3; N,9.0%.

Attempted reaction of iodo-carbonylphenylisocyanide-cyclopentadienyliron with triphenylphosphine. - Triphenyl-phosphine (0.87 g., 0.0033 mole) was added to a solution of iodo-carbonylphenylisocyanidecyclopentadienyliron (1.23 g., 0.0033 mole) in benzene (60 ml.). The mixture was stirred at

reflux for 3 hr. After cooling, the solvent was removed in vacuo. The residue was dissolved in a minimum of benzene and chromatographed. Ligroin/benzene (9:1) eluted triphenylphosphine. Ligroin/benzene (6:4) eluted iodocarbonylphenylisocyanidecyclopentadienyliron (1.1 g. 89% rec.).

Substitution of iodo-carbonyltriphenylphosphinecyclopentadienyliron with phenylisocyanide. - Phenylisocyanide (0.2 g. 2 mmole) was added to a solution of iodo-carbonyltriphenylphosphinecyclopentadienyliron (1.08 g., 2 mmole) in benzene (60 ml.) and the mixture stirred at reflux for 3 hr. The mixture was cooled and the solvent removed in vacuo. The residue was dissolved in a minimum of benzene and chromatographed. Ligroin/benzene (9:1) eluted trace amounts of unreacted phenylisocyanide. Ligroin/benzene (7:3) eluted three bands. The first band afforded brown crystals, m.p. 108°C (48 mg., 0.12 mmole) of iodo-carbonylphenylisocyanidecyclopentadienyliron. The second band gave iodo-carbonyltriphenylphosphinecyclopentadienyliron (0.1 g., 9% rec.). The final band eluted from the chromatogram afforded deep red crystals m.p. 104°C (0.38 g., 0.84 mmole) of iodo-bis(phenylisocyanide) cyclopentadienyliron.

Reduction of iodo-carbonylphenylisocyanidecyclopentadienyliron with sodium borohydride. - Iodo-carbonylphenylisocyanidecyclopentadienyliron (2.17 g., 5.7 mmole) and sodium borohydride (0.5 g.) were stirred in refluxing tetrahydrofuran

(40 ml.) for 3 hr. The mixture was cooled and shaken with water (60 ml.). After filtering through keiselguhr, the mixture was extracted with benzene (3 x 50 ml.), dried over sodium sulphate, evaporated to small bulk and chromatographed. Ligroin eluted ferrocene (170 mg. 16%) which was identified by m.p. and infrared spectrum. Ether/ligroin (1:9) eluted red crystals of bis(carbonyl-μ-carbonylcyclopentadienyliron) (170 mg., 8.4%) which was also characterised by its m.p. and infrared spectrum. Further elution with ether/ligroin (1:9) afforded a third band which gave a red solid which crystallised from methylene chloride/ligroin as deep red crystals, m.p. 131°C (115 mg., 5.3%).

Bis[carbonyl-μ-(carbonyl-phenylisocyanide)cyclopentadienyliron] absorbs in the infrared at 2004 $cm.^{-1}$, 1949 $cm.^{-1}$, 1795 $cm.^{-1}$ and 1704 $cm.^{-1}$ (all strong; KI).

Found: C,55.7; H,3.0; N,3.1;

$C_{20}H_{15}Fe_2NO_3$ requires: C,56.0; H,3.5; N,3.3%.

Elution with ether gave a red gum (10 mg.) which showed maxima in the infrared at 2155 $cm.^{-1}$ (medium), 2020 $cm.^{-1}$,

showed maxima in the infrared at 2155 $cm.^{-1}$ (medium), 2020 $cm.^{-1}$,

(1972 $cm.^{-1}$ (both strong) 1786 $cm.^{-1}$ (V. weak), 1692 $cm.^{-1}$ (strong)

Reaction of iodo-carbonylphenylisocyanidecyclopentadienyliron with sodio-dicarbonylcyclopentadienyliron. - A solution of bis(carbonyl-μ-carbonylcyclopentadienyliron) (0.88 g.,

2.5 mmole) in benzene (50 ml.) was added to 1% sodium amalgam (5.5 g., 0.005 g. atom) and the mixture stirred vigorously for 13 hr. at room temperature. The mixture was filtered rapidly through kieselguhr and added to iodo-carbonylphenylisocyanidecyclopentadienyliron (1.87 g., 5 mmole). The mixture was stirred for 2 hr. at room temperature. The solvent was removed in vacuo and the residue dissolved in a minimum of benzene and chromatographed. Ligroin eluted ferrocene (32 mg., 0.17 mmole), identified by m.p. and infrared spectrum. Benzene/ligroin (6:4) eluted bis(carbonyl-μ-carbonylcyclopentadienyliron) (0.1 g., 11% rec.). Ether eluted iodo-carbonylphenylisocyanidecyclopentadienyliron (0.16 g., 8% rec.).

Substitution of iodo-tricarbonylcyclopentadienylmolybdenum with phenylisocyanide. - Phenylisocyanide (4.12 g., 0.04 mole) was added to a solution of iodo-tricarbonylcyclopentadienylmolybdenum[124] (1.8 g., 5 mmole) in tetrahydrofuran (50 ml.), and the mixture stirred at reflux for 3½ hr. After allowing to cool, the solvent was removed in vacuo and the residue extracted with benzene and chromatographed. Ligroin / bbenzene (9:1) eluted unreacted phenylisocyanide. Ligroin/benzene (1:1) eluted a red band which afforded red needles on recrystallisation from chilled pentane, m.p. 75°C (0.42 g., 19%) Iodo-di(carbonyl)phenylisocyanidecyclopentadienyl molybdenum shows maxima in the infrared at 2141 $cm.^{-1}$ (strong), 2070 $cm.^{-1}$ (medium),

2004 cm.$^{-1}$ (strong), and 1942 cm.$^{-1}$ (strong) ($CCl_4$)

Found: C,37.0; H,2.4; N,3.3; O,7.0;

$C_{14}H_{10}IMoNO_2$ requires : C,37.6; H,2.3; N,3.1; O,7.2%.

Substitution of chloro-tricarbonylcyclopentadienylmolybdenum with phenylisocyanide. - Phenylisocyanide (1.5 g., 15 mmole) was added to a solution of chloro-tricarbonylcyclopentadienylmolybdenum[124] (1.4 g., 5 mmole) in tetrahydrofuran (50 ml.) and the mixture stirred at reflux for 4 hr. The orange solid which precipitated on cooling was removed and recrystallised from methylene chloride/ligroin as red needles, m.p. 180°C(dec.), 1.2 g., 45%). Chloro-tris(phenylisocyanide)cyclopentadienylmolybdenum shows maxima in the infrared at 2169 cm.$^{-1}$ (medium) and 2096 cm.$^{-1}$ (strong)

Found: C,63.9; H,3.6; N,8.5;

$C_{26}H_{20}ClMoN_3$ requires: C,64.1; H,4.0; N,8.3%

Substitution of bicyclo[2,2,1]-hepta-2,5-dienetetracarbonylmolybdenum with phenylisocyanide. - Phenylisocyanide (1 g., 0.01 mole) was added to a solution of bicyclo[2,2,1]-hepta 2,5-dienetetracarbonylmolybdenum[105] (0.91 mg., 3.3 mmole) in tetrahydrofuran (30 ml.). The mixture was stirred at reflux for 4 hr. After cooling, the solvent was removed in vacuo. The yellow residue was recrystallised from methylene chloride/ligroin as yellow crystals, m.p. 116-8°C (0.748 mg., 59%). Tetracarbonylbis(phenylisocyanide)molybdenum absorbs in the infrared

at 2160 cm.$^{-1}$ (medium), 2110 cm.$^{-1}$ (strong), 2033 cm.$^{-1}$ (strong), 1905 cm.$^{-1}$ (strong).

Found: N,7.1

$C_{18}H_{10}MoN_2O_4$ requires N,6.8%

Reaction of Tropyliumdicarbonylmolybdenum iodide with phenylisocyanide. - A mixture of phenylisocyanide (3 g. 0.03 mole) and tropyliumdicarbonylmolybdenum iodide (1.4 g., 37 mmole) in tetrahydrofuran (50 ml.) was stirred at reflux for 3 hr. After cooling, the solvent was removed in vacuo. The brown residue was precipitated from methylene chloride by ligroin as a gum (1.32 g.). The infrared spectrum of the gum did not show absorption in either the metal carbonyl or metal isocyanide stretching frequency regions and was not examined further.

Attempted substitution of tricarbonylbenzenechromium with phenylisocyanide. - Phenylisocyanide (3.1 g., 0.03 mole) was added to a solution of tricarbonylbenzenechromium (1.01 g., 5 mmole) in tetrahydrofuran (40 ml.). The mixture was stirred at reflux for 3 hr., cooled and the solvent removed in vacuo. The residue was dissolved in a minimum of benzene and chromatographed. Ligroin eluted first unreacted phenylisocyanide then tricarbonylbenzenechromium (0.91 g., 90% rec.).

Tricarbonyltris(phenylisocyanide)chromium. Phenylisocyanide (5 g., 0.05 mole) was added to a solution of tricarbonyl-

cycloheptatrienechromium[109,129] (0.88 g., 0.004 mole) in benzene (25 ml.). The solution was stirred at reflux until the red colour of the cycloheptatriene complex had disappeared (30 min.). After cooling, the solvent was removed in vacuo and the residue crystallised from chloroform/ethanol as yellow crystals, m.p. (1.6 g., 90%). Tricarbonyltris(phenylisocyanide) chromium absorbs in the infrared at 2155 $cm.^{-1}$ (medium) 2088 $cm.^{-1}$ (strong) 2004 $cm.^{-1}$ (medium) 1905 $cm.^{-1}$ (broad band, strong)

Found C,65.0; H,3.7; N,9.7.

$C_{24}H_{18}CrN_3O_3$ requires C,64.7; H,3.4; N,9.4.

Attempted substitution of tricarbonyltris(phenylisocyanide)chromium with 1,3,5-trimethylbenzene. - Tricarbonyltris(phenylisocyanide)chromium (0.89 g., 2 mmole) was heated in refluxing 1,3,5-trimethylbenzene (25 ml.) for 2 hr. The mixture was cooled and chromatographed. Ligroin eluted 1,3,5-trimethylbenzene, followed by unreacted tricarbonyltris(phenylisocyanide) chromium (0.73 g., 70% rec.).

The reaction was repeated using the same quantities of reactants, and the mixture exposed to ultraviolet irradiation for 14 hr. The starting materials were recovered (51%) unchanged.

Attempted substitution of hexakis(phenylisocyanide) chromium with cyclohepta(1,3,5)triene. - Hexakis(phenylisocyanide) chromium (3.3 g., 5 mmole) and cyclohepta(1,3,5)triene (9.2 g.,

0.1 mole) were stirred at reflux in each of the following solvents (50 ml.);

(a) ethylene glycol dimethyl ether

(b) ethylene glycol diethyl ether

(c) diethylene glycol dimethyl ether.

Cooling and removal of solvent *in vacuo* gave unreacted starting materials (70-90%) in each case.

Reaction of pentakis(phenylisocyanide)cobalt(1) iodide with cyclopentadienyl sodium. - Pentakis(phenylisocyanide)cobalt iodide (7.01 g., 0.01 mole) was added to a solution of cyclopentadienyl sodium (0.03 mole), prepared from sodium (0.69 g., 0.03 g. atom) and excess cyclopentadiene, in tetrahydrofuran (130 ml.). The mixture was stirred at room temperature for 16 hr. After the removal of the solvent *in vacuo*, the residue was extracted with benzene and chromatographed. Extensive decomposition occurred and only one band was obtained from the chromatogram. Benzene eluted a brown band which afforded a gum (0.14 g.), the infrared spectrum of which did not show absorption in the metal isocyanide stretching frequency region, and it was not examined further.

Reaction of pentakis(phenylisocyanide)cobalt iodide with sodio-pentacarbonylmanganese. - Pentakis(phenylisocyanide) cobalt iodide (3.5 g., 5 mmole) was added to a solution of

sodio-pentacarbonylmanganese (0.01 mole) prepared from sodium amalgam (0.01 g. atom sodium) and manganese carbonyl (1.95g., 5 mmole), in tetrahydrofuran (100 ml.). The mixture was stirred for 3 hr. at room temperature. Removal of the solvent in vacuo left a deep red gum which was extracted with benzene and chromatographed. Ligroin eluted manganese carbonyl (0.75 g., 39% rec.). Benzene eluted a brown gum (320 mg.) the infrared spectrum of which showed maxima at 2062 $cm.^{-1}$, 2033 $cm.^{-1}$, 2000 $cm.^{-1}$, and 1976 $cm.^{-1}$ and weak absorption at 2193 $cm.^{-1}$ and 2165 $cm.^{-1}$ ($CCl_4$). The gum could not be obtained pure for analysis and was not examined further.

Reaction of bis(u-carbonyl-carbonylbicyclo-[2,2,1]-hepta-2,5-dienecobalt) with phenylisocyanide. - Phenylisocyanide (2.02 g., 0.02 mole) was added to a solution of bis(u-carbonyl-carbonylbicyclo-[2,2,1]-hepta-2,5-dienecobalt) in tetrahydrofuran (50 ml.) and the mixture stirred at 40-60° for 2 hr. After cooling, the solvent was removed in vacuo. The residue was extracted with benzene and chromatographed. Ligroin eluted phenylisocyanide. Ligroin/benzene (1:1) eluted bis(u-carbonyl-carbonylbicyclo-[2,2,1]-hepta-2,5-dienecobalt)(53 mg. 2% rec.). Benzene eluted a black solid (94 mg.) the infrared spectrum of which showed only extremely weak absorption in the metal carbonyl and metal isocyanide stretching frequency regions. The compound was not examined further.

Reaction of sodio-tetracarbonylcobalt with phenylisocyanide. - Phenylisocyanide (10 g., 0.1 mole) was added to a solution in tetrahydrofuran (100 ml.) of sodio-tetracarbonylcobalt, prepared from 2% sodium amalgam (0.02 g. atom sodium) and bis(tetracarbonylcobalt) (2.63 g., 0.01 mole). The mixture was stirred at reflux for 2 hr., cooled and iodomethane (7 g., 0.05 mole) added dropwise. The mixture was stirred for 1 hr. at room temperature. After removal of the solvent *in vacuo*, the residue was extracted with benzene (3 x 5 ml.) and chromatographed. Ligroin eluted phenylisocyanide. Elution with benzene afforded a brown solid (0.14 g.) which did not show absorption in either the metal carbonyl or metal isocyanide stretching frequency regions of the infrared and was not examined further.

Reaction of di(cyclopentadienyl)nickel with phenylisocyanide. - Phenylisocyanide (3.0 g., 0.03 mole) was added to a solution of di(cyclopentadienyl)nickel (1.37 g., 8.9 mmole) in tetrahydrofuran (20 ml.). A yellow precipitate formed immediately The mixture was stirred for 30 min. at room temperature, filtered, and the residue washed with ligroin (3 x 20 ml.) to leave tetrakis(phenylisocyanide)nickel (2.6 g.), m.p. 202°C [Lit.[130,131], 202-204°]. Removal of the solvent *in vacuo* from the filtrate gave a further yield of the nickel isocyanide complex (0.6 g.) (Total yield; 3.2 g., 78%).

Di(phenylisocyanidecyclopentadienylnickel). - Tetrakis-phenylisocyanidenickel (1.17 g., 2.5 mmole) was suspended in dry benzene (50 ml.). Di(cyclopentadienyl) nickel (0.47 g., 2.5 mmole) was added to the suspension, and the mixture heated at reflux with stirring for 3 hr. The solution changed from green to red. The mixture was cooled and the solvent removed in vacuo. The residue was dissolved in benzene and chromatographed. Benzene/ligroin (1:1) eluted di(phenylisocyanidecyclopentadienylnickel) (0.65 g., 57%) which crystallised from chilled pentane as deep red plates, m.p. 91°C.

Found: C,63.1; H,4.9; N,6.1;

$C_{24}H_{20}N_2Ni_2$ requires: C,63.5; H,4.6; N,6.2%.

The infrared spectrum shows absorption at 2174 $cm.^{-1}$ ($C_2H_4Cl_2$) in the metal isocyanide stretching frequency region.

# EXPERIMENTAL

## PART II

Tricarbonylpyrrolylmanganese. - Pyrrole (12 ml.) was added to a solution of manganese carbonyl (3.9 g., 0.01 mole) in 100-120 ligroin* (45 ml.). The mixture was stirred at reflux for 14 hr., cooled and chromatographed. Ligroin eluted manganese carbonyl (1.9 g., 47%). Ligroin/benzene (4:1) eluted excess pyrrole. Further elution with the same solvent mixture gave tricarbonylpyrrolylmanganese, (1.4 g., 66%) which crystallised from pentane as pale orange needles, m.p. 41°C [Lit.; 40.5-41°C][121].

* The 100-120° ligroin was rigorously purified by washing in turn with conc. sulphuric acid, acidic potassium permanganate solution, and water, dried over calcium chloride and distilled from sodium.

Reaction of bromo-pentacarbonylmanganese with pyrrolyl potassium. - Pyrrole (0.7 g., 11 mmole) was added dropwise to a stirred suspension of potassium (0.39 g., 0.01 g. atom) in tetrahydrofuran (20 ml.). The mixture was stirred at room temperature until all the potassium had reacted (ca. 5 hr.) Bromo-pentacarbonylmanganese (2.75 g., 0.01 mole) in tetrahydrofuran (40 ml.) was added to the white suspension, and the mixture heated at reflux for 4 hr. with stirring. The mixture was cooled and the solvent removed *in vacuo*. The residue was extracted with benzene and chromatographed. Ligroin eluted manganese carbonyl (0.77 g.). Ligroin/ benzene (4:1) eluted excess pyrrole followed by tricarbonylpyrrolylmanganese (0.18 g.,

9%) m.p. 41°C [Lit. 40.5-41°C].

Attempted reaction of indole with manganese carbonyl. - A mixture of indole (2.34 g., 0.02 mole) and manganese carbonyl (3.9 g., 0.01 mole) were stirred at reflux in 100-120 ligroin for 5 hr. The mixture was cooled and chromatographed. Ligroin eluted manganese carbonyl (2.1 g., 55%). Further elution with more polar solvents gave only unreacted indole which spread over the chromatogram and proved difficult to recover.

Reaction of indolyl potassium with bromo-pentacarbonyl-manganese. - Bromo-pentacarbonylmanganese (2.9 g., 0.01 mole) was added to a suspension in tetrahydrofuran (60 ml.) of indolyl potassium, prepared from potassium (1.54 g., 0.01 mole) and indole (1.16 g., 0.01 mole). The mixture was stirred at room temperature for 3 hr. After the removal of the solvent in vacuo, the residue was dissolved in benzene and chromatographed. Ligroin eluted manganese carbonyl (0.84 g., 29%). Ligroin/benzene (1:1) eluted a yellow solid (0.16 g.), which was contaminated by indole Examination of the infrared spectrum of the mixture showed the presence of metal-carbonyl peaks. Careful chromatography on more active alumina (1 hour deactivated) failed to separate the mixture. Sublimation also failed to assist in purification due to the volatility of indole. The yellow solid was not examined further.

Tricarbonyl-2-methylpyrrolylmanganese. - 2-Methylpyrrole (4.9 g., 0.06 mole) was added to a solution of manganese carbonyl (0.97 g., 2.5 mmole) in ethylene glycol diethyl ether (20 ml.) and the mixture stirred at reflux for 12 hr. After cooling the solvent was removed in vacuo. The residue was dissolved in a minimum of benzene and chromatographed. Ligroin eluted manganese carbonyl (0.5 g., 51%). Ligroin/benzene (4:1) afforded a yellow oil (247 mg.) which was rechromatographed. Ligroin/benzene (4:1) eluted tricarbonyl-2-methylpyrrolylmanganese (0.064 g., 12%) which was purified by sublimation onto a cold probe at high vacuum ($10^{-3}$ mm. Hg.). Tricarbonyl-2-methylpyrrolylmanganese absorbs in the metal-carbonyl stretching frequency region of the infrared at 2056 $cm.^{-1}$ and 1969 $cm.^{-1}$ (both strong; $CCl_4$)

Found N,6.2;

$C_8H_6MnNO_3$ requires: N,6.4%

Reaction of pyrrole-2-aldehyde with manganese carbonyl. - Pyrrole-2-aldehyde (1.9 g., 0.2 mole) was added to a solution of manganese carbonyl (0.97 g., 2.5 mmole) in ethylene glycol diethyl ether (30 ml.) and the mixture stirred at reflux for 14 hr. After cooling, the solvent was removed in vacuo. The residual black solid was extracted with benzene and chromatographed. Elution with benzene gave only a trace of manganese carbonyl. A black material was absorbed on the chromatogram and could not be eluted with normal organic solvents.

Attempted reaction of N-methylpyrrole with manganese carbonyl. - N-methylpyrrole (10 g., 0.06 mole) was added to a solution of manganese carbonyl (3.9 g., 0.01 mole) in 100-120 ligroin (50 ml.) and the mixture stirred at reflux for 18 hr. The mixture was cooled and chromatographed. Ligroin eluted unreacted manganese carbonyl (3.6 g., 92%). Elution with benzene gave only N-methylpyrrole.

Reaction of pyrrole with molybdenum carbonyl. - A mixture of pyrrole (5.36 g., 0.08 mole) and molybdenum carbonyl (5.28 g., 0.02 mole) were stirred in refluxing diethylene glycol dimethyl ether (50 ml.) for 12 hr. After cooling, the mixture was filtered through kieselguhr. The yellow filtrate decomposed rapidly on exposure to air. Removal of the solvent in vacuo left molybdenum carbonyl (0.7 g., 13%).

Reaction of pyrrolylpotassium with molybdenum carbonyl. - Molybdenum carbonyl (5.28 g., 0.02 mole) was added to a suspension of pyrrolylpotassium (0.03 mole) in tetrahydrofuran (60 ml.), prepared from pyrrole (2.97 g., 0.045 mole) and potassium (1.17 g., 0.03 g. atom). The yellow mixture was stirred at reflux for 12 hr. After cooling to -20°C, acetic acid (2 g., 33 mmole) was added and the mixture allowed to warm up to room temperature with stirring (circa 1 hr.). Filtration gave a yellow solid, which decomposed on exposure to air. The solid was added to carbon tetrachloride (50 ml.) and the solution stirred at room

temperature for 15 min. Removal of the solvent *in vacuo* gave molybdenum carbonyl (0.24 g., 4%).

Reaction of pyrrolyl potassium with bis(triphenylphosphine)nickel(II) bromide. - Bis(triphenylphosphine)nickel(II) bromide (3.69 g., 5 mmole) was added to a suspension of pyrrolyl potassium (0.01 mole) in tetrahydrofuran (50 ml.), prepared from pyrrole (0.96 g., 0.015 mole) and potassium (0.39 g., 0.01 g. atom). The mixture was stirred at reflux for 3 hr., cooled, and the solvent removed *in vacuo*. The residue was extracted with benzene and chromatographed. Triphenylphosphine (0.73 g., 2.8 mmole) was the only product eluted from the chromatogram.

Reaction of pyrrolylpotassium with bis(triphenylphosphine)nitrosylnickel bromide.- Bis(triphenylphosphine) nitrosylnickel bromide[125] (2.4 g., 3 mmole) was added to a suspension of pyrrolyl potassium (3 mmole), in tetrahydrofuran (50 ml.), prepared from pyrrole (0.92 g., 0.015 mole) and potassium (0.13 g., 0.003 g. atom). The mixture was stirred at reflux for 3 hr., cooled, and the solvent removed *in vacuo*. The residue was extracted with benzene and chromatographed. Elution with normal organic solvents gave only triphenylphosphine (0.33 g., 1.2 mmole).

Attempted reaction of bis(tetracarbonylcobalt)mercury with pyrrole. - A mixture of pyrrole (1.9 g., 0.06 mole) and

bis(tetracarbonylcobalt)mercury (2.7 g., 0.005 mole) were stirred in refluxing tetrahydrofuran (50 ml.) for 3 hr. After cooling, the solvent was removed in vacuo to give unchanged bis(tetracarbonylcobalt)mercury (1.8 g., 65%).

Cyclopentadienyl-pyrrolyliron. - Iodo-dicarbonylcyclopentadienyliron (3 g., 0.01 mole) was added to a suspension of pyrrolyl potassium (0.01 mole) in benzene, prepared from pyrrole (0.78 g., 0.012 mole) and potassium (0.39 g., 0.01 g. atom). The mixture was stirred at reflux for 3 hr., cooled and the solvent removed in vacuo. The residue was extracted with benzene and chromatographed. Ligroin eluted ferrocene (0.14 g., 7%), identified by m.p. and infrared spectrum. Benzene eluted unreacted iodo-dicarbonylcyclopentadienyliron (0.11g., 3%). Elution with ether afforded orange crystals of cyclopentadienyl-pyrrolyliron (0.41 g., 22%) m.p. 108°C.

Found: C,57.7; H,5.0; N,7.4;

$C_9H_9NFe$ requires: C,57.8; H,4.9; N,7.4%

The ultraviolet absorption spectrum shows one peak at 124 mμ ($\epsilon$ = 14,750).

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